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AMERICAN LEATHER CHEMISTS ASSOCIATION

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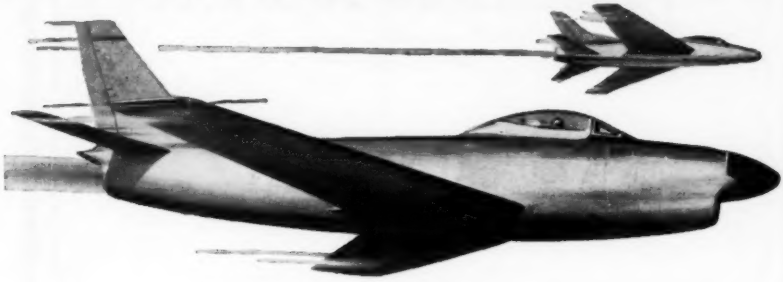

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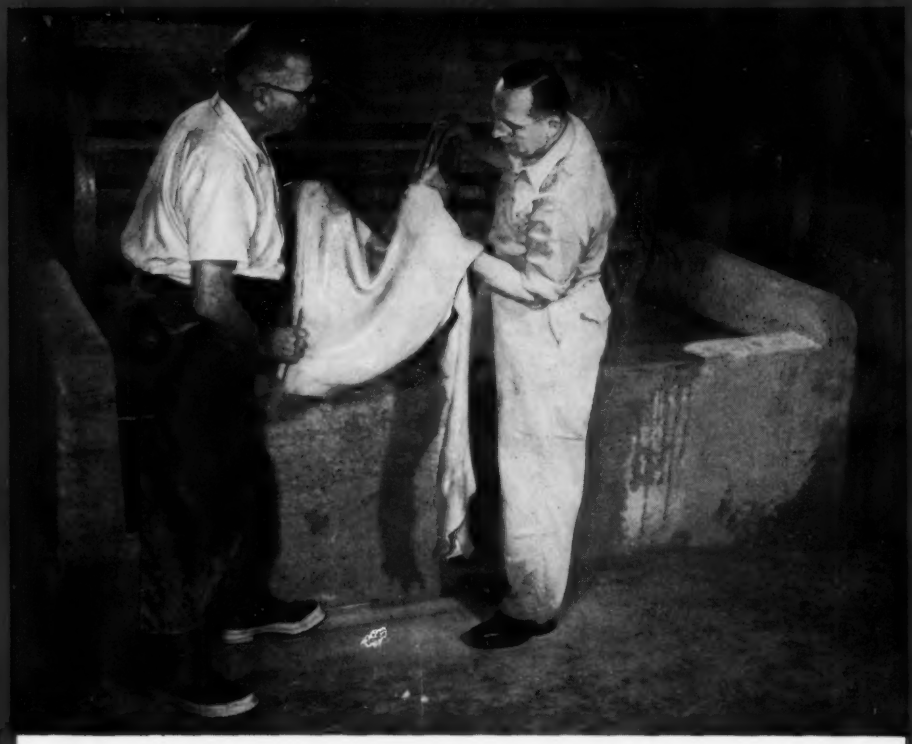

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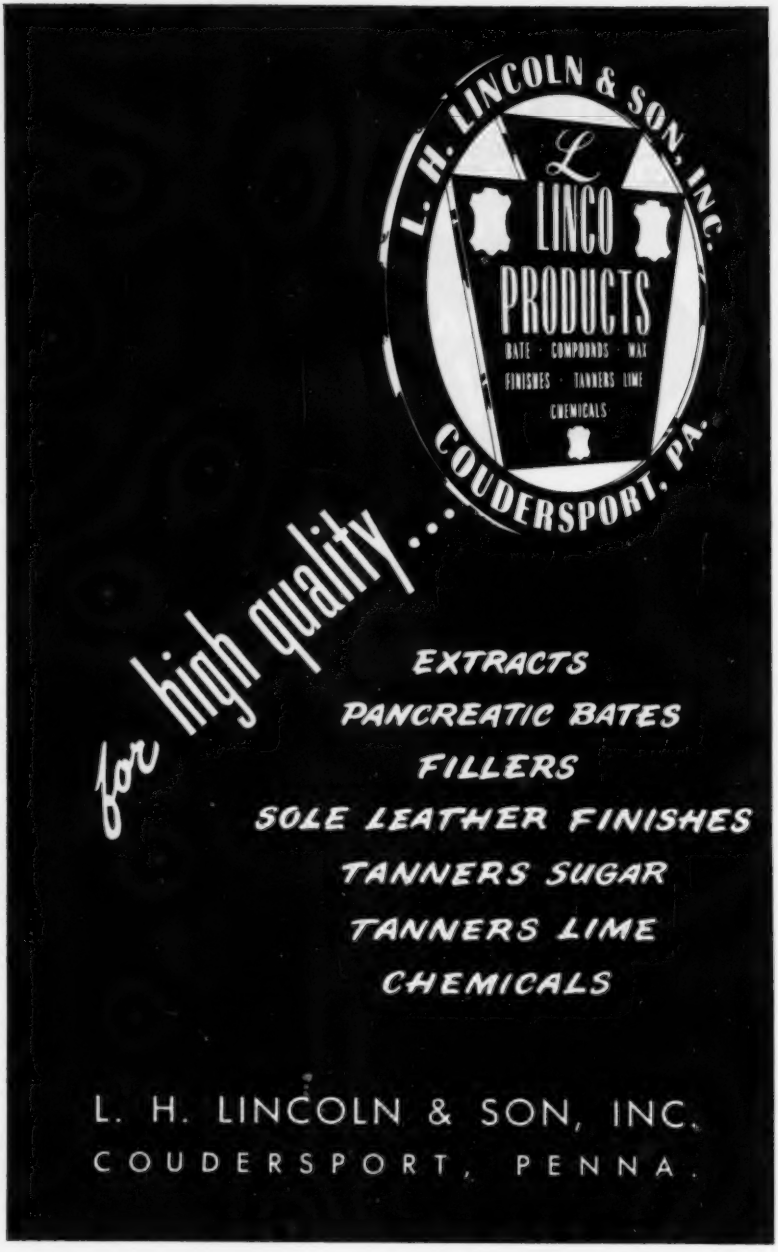
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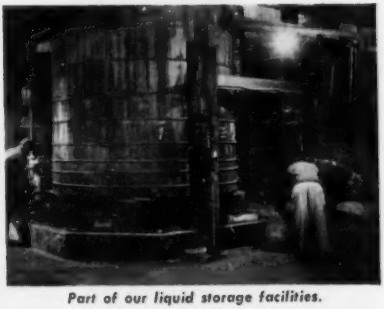

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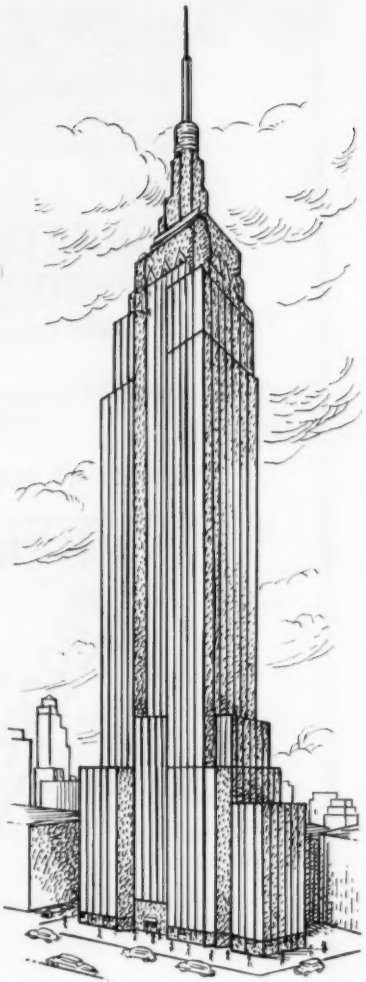

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George J. Katz, 4 Roundy Road, Marblehead, Massachusetts.
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Manuel Koutrakis, 25 Summit Terrace, Peabody, Massachusetts.
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Wilbur Peterson, Salem Oil and Grease Company, 60 Grove Street, Salem, Massachusetts.
John H. Ramsden, 32 Hampden Street, Swampscott, Massachusetts.
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WILLIAM O. BARRETT -- OBITUARY

William H. Barrett, a long time active member of the American Leather Chemists Association, passed away August 4, 1955 at the age of 77. Mr. Barrett was President and founder of Barrett and Company, Newark, New Jersey.

Mr. Barrett had been confined to his home in Wellsville, Pennsylvania for the past several years.

During his active life, Mr. Barrett was a leader in the Industry, he was a most progressive industralist and many of the new developments in tanning and leather had inception in his tannery.

Mr. Barrett took an active part in the functions of the Tanners' Council and served two years as President.

Mr. Barrett will be missed by his many friends and associates, he is survived by his widow, Ethel Beard Barrett, a daughter, Mrs. James Beard and a son, Hunter L. Barrett and five grandchildren.

FRED O'FLAHERTY

ARTHUR SAUER -- OBITUARY

Arthur Sauer, an active member of the Association, passed away, June 18, 1955 at his summer home in Lake Mohawk, New Jersey.

Mr. Sauer was born, June 4, 1892 in Milwaukee where he received his education and became associated with his father in the tanning industry. Here he received good training in the practical aspect of the industry.

Mr. Sauer later became interested in the marketing of quebracho extracts and for thirty-five years was with the River Plate Corporation and its predecessors.

During the past several years, Mr. Sauer was associated with Tanimex Corporation where he served as a Vice President.

Since 1935 Mr. Sauer has been an active member of the A.L.C.A. His passing is mourned by a vast host of friends.

Mr. Sauer is survived by his widow, Mrs. Sauer, a brother and a sister.

FRED O'FLAHERY

MINUTES OF MEETING OF DELEGATES OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS' SOCIETIES

A meeting of the Council of Delegates of the International Union was held on Monday, August 1st. in The Royal Institute of Technology, Stockholm, Sweden, with Dr. K. H. Gustavson, President, in the Chair and 35 other delegates present.

Minutes. The minutes of the Barcelona meeting were outlined by the Hon. Secretary and accepted as correct.

Hon. Secretary's Report. The Hon. Secretary presented his report which dealt with the formation and work of the Technical Standing Committee. This committee had been asked to give some information to the International Council of Tanners on the effect of fillers used in shoe construction on the breathing properties of leather. With the help of Dr. Mitton the report was prepared and presented to the Tanners Council.

A request had been received from the Indian Society of Leather Technologists, and details had been sent to Dr. Banerjoe, the Secretary. It was hoped that this Society would join the Union.

Arising from this report, Mr. G. H. W. Humphreys suggested that the final report might be published or circulated in some form, and the Secretary was instructed to take up this matter with the International Tanners Council.

Financial Report. Prof. Burton presented the financial report for which he was thanked. It was agreed to adopt the suggestions of the Executive Committee that

(a) the subscriptions for 1956-57 should remain as at present, i. e. £6, per official delegate.

(b) financial assistance might be given to Host Societies of Conferences as stated in the Executive Committee Report.

Venue of 1957 *Conference.* The Executive Committee's recommendation that the offer of the Italian Society to hold the 1957 Conference in Italy be accepted, with the best thanks of the Union.

Election of 1st Vice President. The President said it would be fitting to select a 1st. Vice President from the Italian Society and he had pleasure in submitting the name of Dr. G. A. Bravo. This met with complete approval, and Dr. Bravo thanked the Council for the honour of being selected for that office.

Election of Co-opted Members. A member Society of the Union had submitted a proposal that the Executive Committee be enlarged so as to include more co-opted members. After a short discussion, the question was put to the vote which resulted in

For enlargement	9
Against enlargement	18

The size of the Executive therefore stands as at present. For the two co-opted members, three proposals were put forward, Mr. van Vlimmeran, Dr. Chambard and Prof. Grassmann. A ballot was taken for which Dr. Mitton acted as Scrutineer.

The ballot results were

Prof. W. Grassmann	28
Dr. P. Chambard	22
Mr. van Vlimmeran	19

Prof. Grassmann and Dr. Chambard were therefore declared elected.

The meeting then terminated.

Cycle Strain Tester for Leather*

By T. J. KILDUFF and J. R. KANAGY

National Bureau of Standards
Washington 25, D. C.

ABSTRACT

A machine which applies cyclic strain for the testing of shoe upper leather is described. Results showing the influence of load and cyclic strain on the endurance of the specimens under test are given. The test detects differences in tannage, grease content, and deterioration produced by accelerated aging.

1. INTRODUCTION

Shoe upper leather generally fails by cracking in the vamp** area of the shoe. The cause of this failure is the continuous flexing of this part of the shoe in walking. This flexing action produces tension and compressive stresses. As

*This report is made as a part of the Leather Research Program sponsored by the Research and Development Division, Office of the Quartermaster General, Department of the Army. This program is under the Advisory Direction of the National Research Council.

**The vamp is the area of the shoe between the toe and the instep.

the vamp area of the shoe is bent when the foot is lifted, a compression stress is applied to the leather. Initially, the compression stress placed on the leather is the most important. However, as the shoe conforms to a definite set governed by the foot and walking style of the wearer, the tension stress applied as the weight of the body is placed on the foot at the completion of a step also becomes important. The loss of grease and the accumulation of dirt on the vamp tend to accelerate and magnify the effects of these stresses.

To evaluate the ability of upper leather to meet the type of conditions produced in a shoe vamp, a test in which a compression-tension cycle is imposed was applied. Such a test has been used for the evaluation of tire cord [1]. The application of this principle to the development of a testing machine and some of the results obtained are presented in this report.

2. Constant Average Strain Machine

The first machine designed for this work was similar to the one used for testing tire cord [1]. Sketches of the design are shown in figures 1 and 2. It

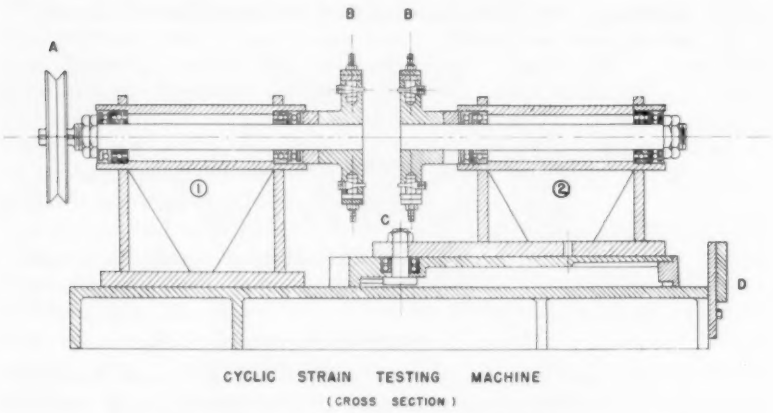

FIGURE 1.—Cross section of the cyclic strain machine.
A—Pulley; B—Rotary disks; C—Axis; D—Platform

consists of two rotary disks, B, which are mounted coaxially on separate assemblies. One of these assemblies, 2, was placed on an axis, C, so that the disk could be skewed with respect to the other by a definite amount by means of the calibrated screw, E. Assembly 2 was mounted on a movable platform D so that the distance between the wheels might be adjusted as desired. The other assembly, 1, was coupled to a motor through A.

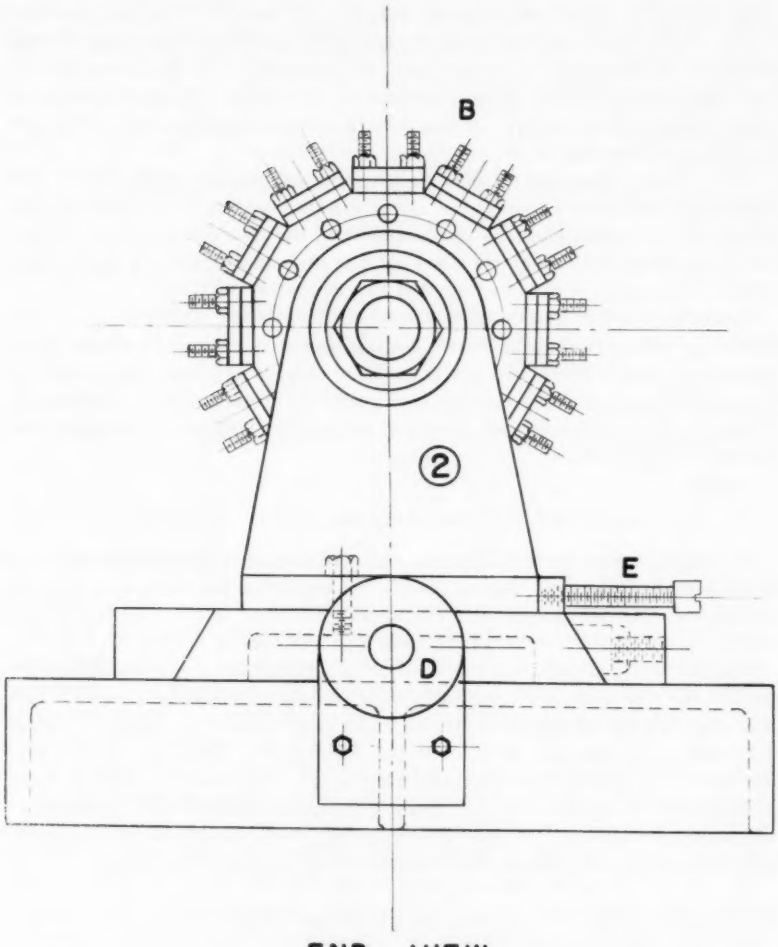

FIGURE 2.—End view of the cyclic strain machine.
B—Rotary disk; E—Calibrated screw; D—Movable platform.

With the disks 1 inch part, specimens of leather ½ inch by 3 inches are mounted across the rims of the disks. This couples them together. Twelve specimens are equally spaced over the circumference of the disks. The specimens are clamped while the disks are parallel or in unskewed position. Disk 2 which is mounted on the axis is then turned a definite amount to give an

angular displacement with respect to disk 1 and locked in the new position. If the coupled disks are then rotated, the leather specimens must pass through positions of longitudinal compression and extension, passing, respectively, through the maxima of these positions at the points where the disks are closest and farthest apart. In this way, a compression-tension cycle is produced in the leather.

The angular displacement used to give the specimens a cyclic strain was calibrated in terms of increase of linear displacement. The arithmetic sum of this displacement and any displacement of the movable platform D from its initial position in which the disks are one inch apart gives the total tensile strain. The speed of the machine was approximately 1700 rpm.

Since leather has a very high permanent set (60 to 70 per cent), it was found to be impossible to maintain a stress on the specimens by means of the procedure used. When the machine is set to give the specimen a definite cyclic strain, only a slight recovery occurs and the stress is almost immediately relieved. Since the specimen does not recover from strain, it does not pass through a cyclic strain.

3. Constant Rate of Average Strain Machine

An attempt was made to operate the machine at a definite setting for a short period of time and then to change the setting to put more strain on the specimens. The specimens were examined from time to time for cracks and the end point of the test was taken when the specimens broke.

Manual manipulation was found to be unsatisfactory and it was decided to modify the test so that a constant rate of elongation could be applied. This was achieved by an assembly of reduction gears which increased the linear displacement at the rate of ⅛ inch per 9.5 minutes. However, at this rate the leather specimens were virtually torn apart. The test thereby consisted principally of a measure of the tensile properties rather than a measure of the resistance to cyclic strain. The diameter of the pulley on the assembly was changed to give a linear displacement of ⅛ inch per 16 minutes.

3.1 *Results of Tests at Constant Rate of Average Strain*

The general procedure used for the tests at a constant rate of average strain is as follows: The machine is started with the disks at zero angular displacement. The linear displacement mechanism is started simultaneously with the starting of the machine. After running for five minutes with a linear displacement only, the desired cyclic strain is applied. The displacement is allowed to proceed until the desired average strain is reached. The test continues until there is an over-all test period of 2 hours.

Results obtained with vegetable-tanned leather using this procedure are shown in table 1. The data given include the number of specimens broken

TABLE 1.

Results Obtained by Applying Constant Rate of Average Strain Testing Procedure to Vegetable-Tanned Leather

Test	Average strain	Cyclic strain	Number of specimens broken	Loss in tensile strength of specimens unbroken in test
	%	%		%
	Group 1. Average Strain Constant, Cyclic Strain Varied			
1	20	7	0	7.4
2	20	10	0	4.4
3	20	13	3	18.3
4	20	16	7	24.8
	Group 2. Average Strain Varied, Cyclic Strain Constant			
1	15	10	0	1.8
2	20	10	0	6.6
3	25	10	2	13.2
4	30	10	1	19.9
	Group 3. Average Strain Varied, Cyclic Strain Varied, Maximum Strain Constant			
1	30	5	0	1.6 gain
2	28	7	1	2.6
3	25	10	1	4.7
4	20	15	1	8.9

at the end of the test and the percentage loss in tensile strength of the specimens that remained unbroken. The specimens for these tests were selected from blocks in such a way as to compensate as much as possible for hide variations. Twelve specimens were used in each test. The residual tensile strength of the specimens that remained unbroken at the end of the test were compared with that of a set of control specimens.

The results given in table 1 show that increasing the total strain on the leather specimens increases the number of specimens broken during the test and the loss in tensile strength of those unbroken in the test. A further examination of the table indicates that the increase in the cyclic strain has the greatest effect on increasing the severity of the test. In group 1 where the average strain is held constant and the cyclic strain is increased, the number of specimens broken and the percentage loss in tensile strength of the unbroken specimens are greatest. In group 3 where the maximum strain is constant in all tests the loss in strength of the unbroken specimen increases as the cyclic strain is increased.

In table 2, results obtained with straight chrome-tanned leather are given. It may be observed that the total strain is considerably higher than it was for vegetable-tanned leather in table 1. The chrome leather stretches more than the vegetable-tanned leather. The rate of breakdown increases as the total strain is increased, just as for vegetable-tanned leather. The effects of increase in cyclic strain are similar to those noted above.

TABLE 2

Results Obtained by Applying Constant Rate of Average Strain Testing Procedure to Chrome-Tanned Leather

Test	Average strain	Cyclic strain	Number of specimens broken	Loss in tensile strength of specimens unbroken in test
	%	%		%
	Group 1. Average Strain Constant, Cyclic Strain Varied			
1	48	7	6	20.2
2	48	10	8	41.5
3	48	13	9	49.8
4	48	16	9	45.3
	Group 2. Cyclic Strain Constant, Average Strain Varied			
1	35	10	0	15.8
2	40	10	1	28.9
3	45	10	7	37.2
4	50	10	12	All broke in test
	Group 3. Cyclic Strain Varied, Average Strain Varied, Maximum Strain Constant			
1	50	5	1	0
2	48	7	2	12
3	45	10	8	47.9
4	40	15	12	All broke in test

4. Constant Load Machine

The application of the procedure in which the average strain was increased at a definite and constant rate was not considered satisfactory because it was difficult to obtain reproducible results. The resistance of the leathers to the test also depended upon the amount that they could be stretched. Stretchy leathers withstand the test more readily than those which are not easily stretched because the stress is less. For these reasons the machine was redesigned to operate under a constant load. This was accomplished by mounting the assembly on the free riding side (assembly 2) on special linear motion ball bearing bushings. This gives free motion when operating under constant load. An attachment on which weights can be mounted replaced the apparatus that produced a constant rate of strain on the previously modified machine. This machine is shown in figure 3. Under these conditions the stress on a specimen depends upon its position on the machine during the strain cycle and upon the number of specimens carrying the load.

The procedure used with this machine was to start the test at about 1700 rpm. with zero angular displacement and a 25-pound load, which is the minimum load that can be applied because of the weight of the loading mechanism. Immediately after starting the machine the angular displacement setting is made. The machine is permitted to run under these conditions for five

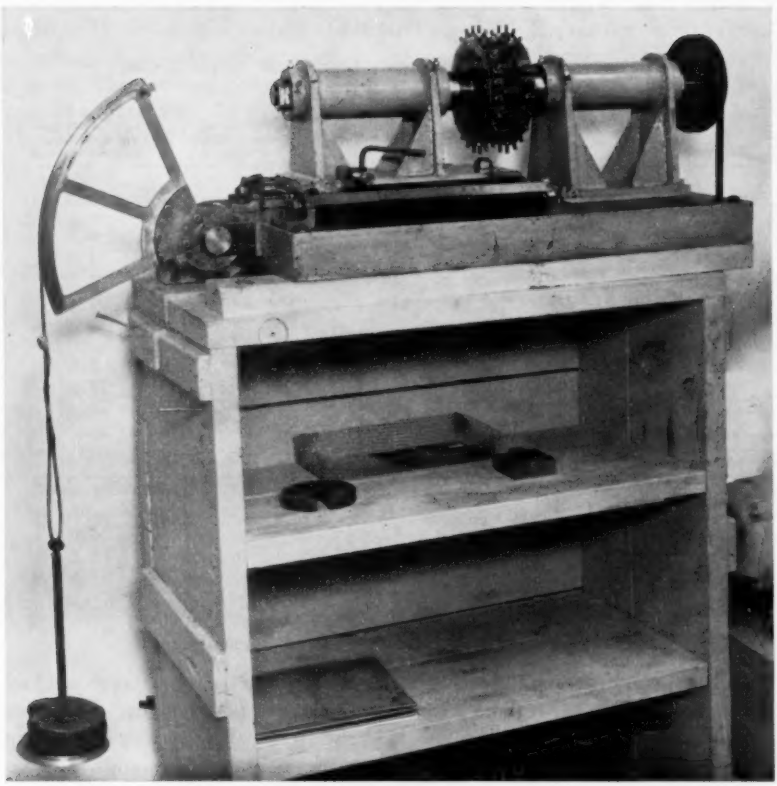

FIGURE 3.—Cyclic strain machine designed to operate under a constant load.

minutes. Weights are then placed on the pan to produce the desired load. The total duration of the test is 3 hours, unless stated otherwise. The percentage of average strain, which is measured by means of a scale fastened to the side of the machine, and the condition of the specimens are recorded every 15 minutes. Since all of the specimens do not break within the 3-hour test period, the tensile strengths of the test specimens that remain unbroken after cyclic strain testing are obtained. This test is evaluated by the number of specimens that break, and the loss in strength of those that do not break. Twelve specimens are used in each test.

4.1 *Results of Tests at Constant Load*

(a) Effect of Load

The effect of load on the breakdown of chrome leather specimens during cyclic strain is shown in table 3. Tests were made with 75–, 100–, and 125–

TABLE 3.

Effect of Load on the Constant-Load Cyclic Strain Testing of Chrome Leather

Test	Load	Cyclic strain	Number of specimens broken	Loss in tensile strength of specimens unbroken in test
	lb.	%		%
		Group 1. 75-Pound Load		
1	75	8	0	6.3
2	75	11	0	11.1
3	75	14	0	24.4
4	75	17	2	31.4
		Group 2. 100-Pound Load		
1	100	8	0	6.5
2	100	11	1	23.6
3	100	14	12	——
4	100	17	12	——
		Group 3. 125-Pound Load		
				Breaking time* hr.
1	125	8		3.0
2	125	11		2.5
3	125	14		1.0
4	125	17		Omitted

*Specimens all broke; therefore, breaking time is given.

pound loads and at angular displacements of such magnitude as to produce cyclic strains of 8, 11, 14, and 17 percent with each of the loads. The effect of load is magnified by the increase in cyclic strain. The rate of breakdown is greatly accelerated by increasing the load from 75 to 125 pounds.

(b) Effect of Time

The breakdown of vegetable-tanned leather specimens versus time in the cyclic strain machine is given in table 4. The specimens were tested with

TABLE 4.

Effect of Duration of Time of Testing on the Breakdown of Vegetable-Tanned Leather in Constant-Load Cyclic Strain Testing

Test	Load	Cyclic strain	Time	Number of specimens broken	Loss in tensile strength of specimens unbroken in test
	Lb.	%	Hr.		%
1	75	14	2	0	10.7
2	75	14	4	0	19.0
3	75	14	6	1	27.4
4	75	14	8	4	40.0

a load of 75 pounds and a cyclic strain of 14 per cent. The results show that the percentage loss in tensile strength is approximately a straight line function of time. The average loss in tensile strength is approximately 5 per cent per hour of exposure to the cyclic strain. Specimens begin to break in the test when the average loss in tensile strength reaches about 27 per cent.

(c) Effect of Grease

The effect of grease on chrome-tanned leather specimens tested in the cyclic strain machine is shown in table 5. Results are given for both stuffed

TABLE 5

Effect of Grease on the Breakdown of Leather in a 3-Hour Constant-Load Cyclic Strain Test

Test	Load	Cyclic strain	Number of specimens broken	Loss in tensile strength of specimens unbroken in test
	Lb.	%		%
	A. Stuffed Leather (25 Per cent Grease)			
1	75	14	0	18.3
2	75	14	0	22.5
3	75	14	0	20.8
4 degreased	75	14	12	——
	B. Fatliquored Leather (9-14 Per cent Grease)			
1	75	14	1	22.6
2	75	14	3	18.9
3	75	14	0	14.2
4 degreased	75	14	12	——

and fatliquored leathers. All degreased specimens broke prior to the end of the 3-hour test; whereas, specimens that contained stuffing grease or fatliquor showed much greater resistance. In two of the three sets of specimens of the fatliquored leather one and three specimens, respectively, broke during the test. There was little difference in the percentage losses in tensile strength for unbroken leather specimens containing either fatliquor or stuffing grease. This indicates that the lower percentage of grease contained in the fatliquored leather is sufficient for lubrication purposes.

(d) Effect of Aging

The effect of aging vegetable-tanned leathers in air at 100°C. and then testing in the cyclic strain machine is shown in table 6. Losses in tensile strengths are calculated by using as a reference the tensile strength of a set of unaged specimens. The gain in tensile strength for specimens aged for 24 and 48 hours was not surprising since results of this type are peculiar to

TABLE 6

Behavior of Vegetable-Tanned Leather in a 3-Hour Constant-Load Cyclic Strain Test After Aging in Air at 100°C.

Test	Time of Aging	Load	Cyclic strain	Number of specimens broken	Loss in tensile strength of specimens unbroken in test
	hr.	Lb.	%		%
1	24	75	14	0	3.7 gain
2	48	75	14	0	2.6 gain
3	72	75	14	0	5.3
4	138	75	14	0	16.4

accelerated aging. Accelerated aging under mild conditions for short periods of time actually increases the apparent tensile strength. After 72 hours of aging, the specimens show a loss in strength in the cyclic strain test.

(e) Evaluation of Tannages

A group of synthetic tannages, described in table 7, was evaluated with the

TABLE 7

Description of Leathers Tanned with Synthetic Tannins

213	Ferro retan.
214	Army retan stuffed with Dermanoil No. 2 and Dermanoil Fat No. 2 [3].
215	Army retan stuffed with blend of natural stuffing material with Dermanoil Fat No. 2 and Dermanoil No. 1 [3].
216	Army retan. Natural stuffing material.
217	Chrome-tanned and retanned with Monsanto 62591.
218	Chrome and Orotan retan; fatliquored upper.
219	Iron chrome, retanned with Monsanto 62591.
220	Sulfonyl chloride, with Monsanto retan 62591.
221	Sulfonyl chloride, with vegetable retan.
222	Sulfonyl chloride, retanned with Rohm and Haas Orotan.
223	Iron-Chemtan; fatliquored.

cyclic strain machine, using a cyclic strain of 14 per cent. The test was started with a 75-pound load and continued under these conditions for 3 hours. If the specimens of a leather sample did not all break under these conditions, another test was made with a new set of specimens and a 90-pound load. The groups that did not break with a 90-pound load were retested, using a third set of specimens and a 100-pound load. The data from these tests are given in table 8.

TABLE 8

Results of Constant-Load Cyclic Strain Test With Leather Prepared From Synthetic Tannages

Tannage No.	Tensile strength of controls	Breaking time in cyclic strain test*	Unbroken specimens		Order of endurance to cyclic stength test
			Tensile strength	Loss in strength	
	lb.	hr.	lb.	%	
		Group I			
		14—Per cent Cyclic Strain: 75-Pound Load; 3-Hour Test			
213	164	2.1	All broken	—	10
214	171	——	140	18	6
215	150	——	132	12	8
216	217	——	175	19	7
217	278	——	240	16	3
218	158	——	110	30	5
219	152	2.2	All broken	—	9
220	153	——	108	29	4
221	164	——	164	0	1
222	185	——	171	8	2
223	137	1.5	All broken	—	11
		Group II			
		14-Per cent Cyclic Strain; 90-Pound Load; 3-Hour Test			
213	164		See Group I.		10
214	171	——	137	20	6
215	150	2.8	All Broken	—	8
216	217	——	156	28	7
217	278	——	239	14	3
218	158	——	114	28	5
219	152		See Group I.		9
220	153	——	130	15	4
221	164	——	185	+11†	1
222	185	——	179	3	2
223	137		See Group I.		11
		Group III			
		14-Per cent Cyclic Strain; 100-Pound Load; 3-Hour Test			
213	164		See Group I.		10
214	171	1.6	All broken		6
215	150		See Group II.		8
216	217	1.5–1.6	All broken		7
217	278	——	162	42	3
218	158	2.1	All broken		5
219	152		See Group I.		9
220	153	2.75	All broken		4
221	164	——	169	+3†	1
222	185	——	174	6	2
223	137		See Group I.		11

* Time required to break all specimens; in other tests no specimens were broken.
† Increased in strength.

From the results of these tests a relative rating was made of the different samples of leather. This rating was based on three factors: the length of time required to break all specimens, the size of the load, and the loss in tensile strength of the unbroken specimens. The ratings are shown in table 9 and are compared with ratings obtained for the same leathers tested in a

TABLE 9

Comparison of Ratings Obtained with Synthetic Tannages with the Flex-tension and Constant-Load Cyclic Strain Machines

Tannage lot No.*	Flex-tension Rank	Cyclic strain Rank
217†	1	3
213	2	10
222	3	2
216	4	7
214	5	6
221	6	1
215	7	8
218	8	5
219	9	9
223	10	11
220	11	4

*Tannage ranked in order of decreasing flexing endurance, No. 1 having the highest endurance.
†For description of tannages, see table 7.

different type of flex-tension testing machine[2]. These comparisons show that, in general, there is little agreement in the relative ratings by the two test procedures. The agreement is little better than would be obtained from a set of random numbers. The rank correlation coefficient for these results is about 0.25, which is not significant.

5. General Discussion

The nature of the effect of the cyclic strain test on leather may be visualized by examining typical specimens tested (figure 4). The result of the tension on an unbroken specimen is to narrow down the part of the specimen between the clamps. A tested, badly torn specimen generally shows that the breakdown occurs at a definite point in the narrowest part of the specimen. Also noticeable are the frayed ends of the fibers broken by the rapid flexing and tension on the specimen.

In making a comparison of two different samples of leather a correction for the stretch of the leather should be considered. The resultant load on the specimens depends upon the width of the cross section. During the test a highly stretchy specimen will become narrower than a less stretchy specimen and, therefore, the effective load is greater. Moreover, as soon as one or more

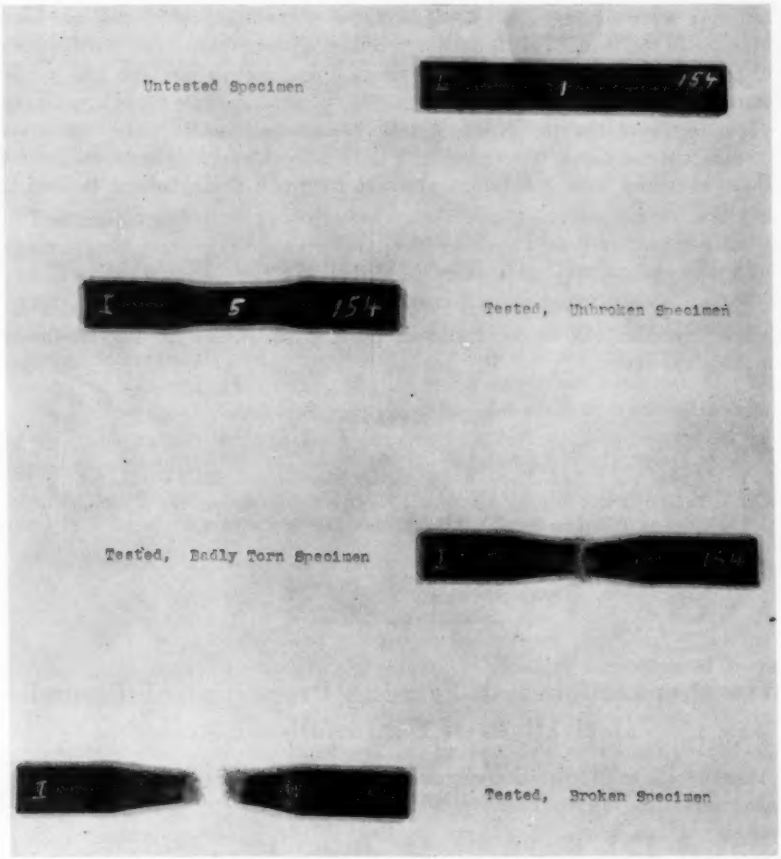

FIGURE 4.—Specimens before and after testing on the cyclic strain machine.

specimens break, the effective load becomes greater. Also, in making comparative tests, specimens should be selected as nearly as possible from the same area of a side of leather so as to minimize variations in their physical characteristics.

6. Conclusions

A machine which applies the principle of cyclic strain has been developed for the testing of upper leather. It was found necessary to operate the test under a constant load to obtain satisfactory results since leather has a low

recovery after strain. The rate of breakdown in the machine increases with increase in the load. This breakdown is directly proportional to the duration of time of testing. The machine detects differences in tannage and grease content. Leathers aged in an oven at 100°C. show a more rapid breakdown dependent upon the time of heating. It shows some promise in the evaluation of different tannages, but the results show a low degree of correlation with those obtained with a different machine in which flexing under tension is applied.

Acknowledgment

The authors wish to express their appreciation to Dr. H. F. Schiefer for major contributions in the design of the apparatus and for suggestions in making the tests.

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The Preparation and Tanning Properties of Phenolic Derivatives of Ligninsulfonic Acid*

Part III. Application of the Phenol Derivative to the Tanning of Heavy Leather

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Abstract

Five mixtures of quebracho and the phenol condensate of a decalcified lignosulfonate material were evaluated by tanning pieces of heavy hide. The mixtures ranged from 0 to 100% condensate. From the methoxyl contents of the resulting leathers it was shown that under the conditions of the experiment, the relative uptake of condensate and quebracho from the tanning liquor was approximately the same as their proportion in the liquor. It was found that the highest leather yield value (on a weight basis) was given by quebracho alone, but the highest degree of tannage was given by a 1:1 mixture of quebracho and con-

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densate. When the amount of condensate in the "blend" was increased in steps from 0 to 75%, thickness yield was unaffected; apparent density was reduced; water absorption was increased; perspiration resistance was slightly reduced, and abrasion resistance was slightly enhanced. The leather tanned with condensate alone was unsatisfactory in weight and thickness yield. However, the properties of the leather tanned with the 1: 1 mixture of condensate and quebracho were close enough to quebracho-tanned leather to justify further evaluation of this blend as a heavy-leather tanning material.

The condensation of ligninsulfonic acid with various phenols and the tanning properties of the resulting derivatives have been described in Parts I and II of this series [1], [2]. It was found that these phenol derivatives were true tanning agents, since they raised the shrinkage temperature of hide and protected it from hydrolysis by trypsin. In addition, a method of application for chrome retanning was worked out. Attention was next turned to the tanning of sole and other heavy leather as an important potential use for the new materials. Tests indicated that the admixture of some proportion of vegetable tannin was necessary for this application. The purpose of the experiment described in this paper was to determine the highest proportion of phenol derivative (or "condensate") to vegetable tannin which could be used in a laboratory scale heavy leather tannage.

Tanning Materials

The condensate to be used in the tanning experiment was prepared in the usual manner from "Lignosol", a spray-dried ligninsulfonate, and phenol. The decationized ligninsulfonic acid was condensed at 125 °C. with an equal weight of phenol in a glass-lined pressure vessel. The unreacted phenol was removed by solvent extraction and the concentrated solution of condensate was neutralized to pH 3.25 with NaOH. The tannin content was determined by a modification of the ALCA Method, using a 30-minute shaking period at 65 °C. and correcting for sulfate liberated from the hide powder. The tannin content of the concentrated solution was 27.1 per cent and the tannin purity was 78.1. The solution contained no insolubles.

A 25 per cent tannin solution of ordinary quebracho was made up for blending with the condensate. Mixing of these two solutions was done at 80°C. The five tanning blends were as follows (proportions are given on a tannin weight basis):

1. 100 per cent condensate
2. 75 per cent condensate, 25 per cent quebracho
3. 50 per cent condensate, 50 per cent quebracho
4. 25 per cent condensate, 75 per cent quebracho
5. 100 per cent quebracho

Design of Experiment

The hide material to be used was a heavy steer bend obtained from a sole leather tanner. The bend had been bated, but the extent of deliming was superficial only.

The natural variability of the hide would have an effect on the reliability of the comparisons to be made between the five tannages, and in order to estimate this effect a suitable design was necessary for sampling the hide.

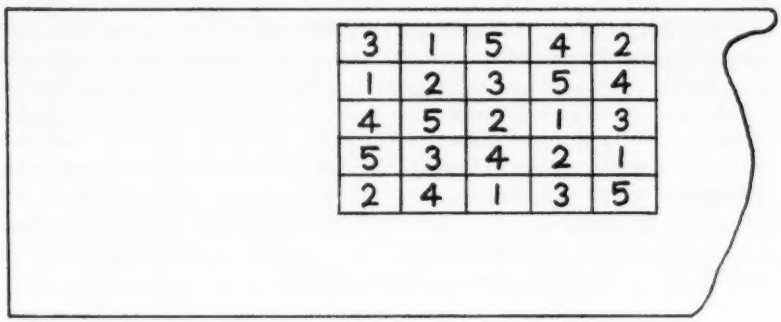

FIGURE 1.

A five-by-five Latin square was chosen. Figure 1 shows the location of the Latin square in the bend. It consists of twenty-five rectangles arranged in five rows and five columns. The numbers 1 to 5 in the rectangles represent the five treatments. Each number appears once in every column and once in every row, but otherwise the distribution of the numbers is completely random.

By using the Latin square technique, one may determine how much of the variance between replicates is attributable to variation in the hide in the direction parallel to the backbone (differences between columns) and perpendicular to the backbone (differences between rows).

Five groups of five pieces of hide were cut from the bend according to this plan. Each piece was five inches by three inches. Numerals were cut into the pieces to show their row, column and treatment number, and a hole was punched into the end of each of them for suspension in the tanning liquor. Their thicknesses were then measured (as described later).

Tanning Method

The hide pieces were washed for 1 hour in cold running water. The five pieces for each treatment were then suspended from a piece of plastic-covered solid copper wire, bent at intervals so as to keep the pieces separated, and at

each end to provide hooks from which the wire could be hung on the rim of a glass battery jar, 4″ x 4″ x 8″ high. The jars containing the suspended hide pieces were then filled with tanning liquor.

The schedule of liquor concentrations and pH values is given in Table I. Each liquor was made up with fresh, concentrated tanning material only. Adjustment of pH was made with sodium hydroxide.

TABLE I

Tanning Schedule

Day No.	Liquor No.	pH	% tannin
0	1	4.8	0.5
1	2	4.7	1.0
2	3	4.6	1.5
3	4	4.5	2.0
4	5	4.2	3.0
7	6	4.0	4.0
10	7	3.5	5.0
14	8	3.4	6.0
21	9	3.4	10.0

After tanning in the jars, the five tannages were treated one by one with a 12.5 per cent tan liquor at pH 3.3, in a rotating tanning cylinder at 100°F., to complete the tanning.

The variation in pH and Barkometer values of the liquors were followed. The pH variation was about the same in the five tannages. The rate of tanning, as measured by the drop in Barkometer value from one day to the next, was slowest for the condensate and fastest for quebracho.

The penetration of the tanning agents into the hide was followed by cutting small wedge-shaped specimens about 1 cm. deep into the edge of each hide piece; washing the specimen, and measuring the depth of penetration from the grain surface and from the flesh surface. It was found that Tannage No. 4 penetrated most slowly. Tanage No. 3 penetrated more quickly than No. 4, and No. 2 more quickly than No. 3.

This observation is probably connected with the particle size of the tanning constituents. The condensate had a marked solubilizing action on quebracho insolubles; the liquors in Tannages 2 and 3 were clear and free from sludge. In the case of No. 4, where there was only one part of condensate tannin to three parts of quebracho tannin, the result was a suspension of the quebracho insolubles, which normally settle out quickly. That the suspended particles were large was evident from the turbidity of the liquor. It may be assumed that the order of decreasing particle size was: Tannages 4, 3, 2, 1.

Treatment of Leather After Tanning

After the leathers had been removed from the last tanning liquor, they were soaked for 1¼ hours in water at 40°C. and then drained for 2½ hours. The thicknesses were measured at this point.

The leathers were next treated as follows, all at 49°C.:

Seven	minutes	in	water
"	"	"	0.3 per cent Na_2CO_3
"	"	"	water
"	"	"	1.5 per cent H_2SO_4
"	"	"	water

Following this treatment the pieces were passed through a wringer to remove excess water; set out smooth with a plate glass slicker; oiled generously on all surfaces with a mixture of equal parts of mineral oil and sulfonated cod oil; and allowed to dry slowly. Finally, the grain surfaces were polished with a dry cloth.

Appearance of Leathers

The color of the quebracho leather (No. 5) was very similar to that of a piece of commercial sole leather on hand.

The color of the condensate leather (No. 1) was a light, rather dull brown.

Tannages 4, 3 and 2, containing increasing amounts of condensate, were progressively duller in color, more grayish, and less pink.

An attempt to estimate the firmness of the pieces indicated that the condensate-tanned leather (No. 1) was appreciably least firm; the firmness then appeared to increase through Nos. 2, 3 and 4. All were much firmer than the commercial sole leather sample.

Chemical Analysis

The ground-up samples were analyzed by the ALCA Methods. The results are shown in Table II.

It is notable that a higher degree of tannage was obtained with the 50–50 blend than with quebracho alone. This result has been confirmed in subsequent experiments and seems to be a consequence of the more stable fixation of the condensate tannin compared to quebracho. Although the leather yield value is higher for quebracho, a larger proportion comes out as "water solubles."

In order to determine the proportion of condensate to quebracho in the combined tannins, the leathers after extraction with petroleum ether and warm water were analyzed for methoxyl [3]. The results are given in Table III.

TABLE II

Chemical Analysis
(Moisture-Free Basis)

Leather No.	1	2	3	4	5
% condensate	100	75	50	25	0
% quebracho	0	25	50	75	100
Pet. Ether Extract, %	9.46	8.20	6.69	7.94	7.30
Water Solubles, %	6.40	6.78	8.79	12.04	15.75
Hide Substance, %	54.6	51.5	50.2	48.7	48.6
Insoluble Ash, %	0.16	0.18	0.16	0.11	0.11
Uncombined tans, %	2.51	3.42	5.56	8.91	13.30
Total Ash, %	0.82	0.58	0.35	0.24	0.20
pH	3.82	3.59	3.50	3.58	3.69
Combined Tans, %	29.38	33.34	34.16	31.21	28.24
Degree of Tannage	53.8	64.7	68.0	64.1	58.4
Weight Yield*	165.8	178.0	185.9	189.0	190.7

*Weight of dry grease-free leather per 100 g. of hide substance.

TABLE III

Methoxyl Analyses and Composition of Tannin

Leather No.	1	2	3	4	5
MeO in extracted leather, %	2.58	2.07	1.43	0.81	0.24
MeO in combined tan, %	8.78	6.21	4.19	2.59	0.85
Condensate in combined tan, %	100.0	67.6	42.1	22.0	0
Quebracho in combined tan, %	0	32.4	57.9	78.0	100.0
Condensate in tanning liquor, %	100.0	71	46	22	0
Quebracho in tanning liquor, %	0	29	54	78	100.0

The value for methoxyl in combined tan was calculated from the values for methoxyl in extracted leather and combined tan in extracted leather. The resulting values were used to calculate the composition of the tannin, as follows: Let x be the percentage of condensate in the combined tannin, and M be the methoxyl value of the combined tannin. Then since the condensate contained 8.78 per cent methoxyl and the quebracho contained 0.85 per cent methoxyl,

$$8.78\,x + 0.85\,(100-x) = 100\,M.$$

The equation is solved for x.

Table III also shows the composition of the tannin in the tanning liquors. A comparison of these values with the composition of the combined tannin shows that the proportion of quebracho to condensate is slightly higher in the combined tannin than in the tanning liquor when there is 54 per cent quebracho or less in the liquor. There are two possible explanations: the hide absorbs quebracho more rapidly than condensate, or the hide has a greater capacity for quebracho.

Physical Tests

The following physical characteristics were determined for each of the five leathers: thickness yield, apparent density, water absorption, stitch tear strength, perspiration resistance, and abrasion resistance.

The thickness yield of each piece of leather was calculated as its average thickness directly after tanning expressed as a percentage of its thickness immediately before tanning. The thickness was measured with a spring-loaded compressometer having a presser foot one inch in diameter loaded to 135 grams.

For the determination of apparent density, a two-inch square was cut from each piece with a steel die. It was dampened with 100 per cent of its weight of water, allowed to condition overnight and compacted in the Carver hydraulic press under a pressure of 375 p.s.i. Each piece was then allowed to dry to constant weight in a conditioned room at 70°F. and 65 per cent R. H.

The length, width, thickness and weight were then measured and the apparent density calculated.

The apparent density specimens were next used for water absorption. The method of the Society of Leather Trades' Chemists was used [4]. It consists of immersing the conditioned, weighed specimen in water for 24 hours, weighing, drying thoroughly, conditioning, and weighing again. The water absorption ("free water" excluding water solubles) was calculated as a percentage of the original weight. The water solubles dissolved during the immersion period were also calculated.

The two-inch squares which had been used for the determination of apparent density and water absorption were further divided as shown in Fig. 2.

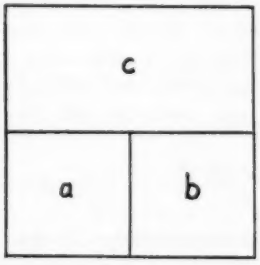

FIGURE 2.

Pieces a, b were tested for abrasion resistance, while piece c was split into grain and flesh splits for perspiration resistance and stitch tear strength tests respectively.

The grain splits were tested for perspiration resistance[5] by soaking in synthetic perspiration for 24 hours at 35°C., drying, and measuring the shrinkage in length of the sample. The extent of curling was also noted. This was repeated for a total of five treatments. Little shrinkage was obtained with any of the samples, in contrast to a commercial sample which showed considerable shrinkage. However, it was noted that the blend tannages curled more than the quebracho tannage, and the straight condensate-tanned leather curled severely. These results were probably connected with the actual amount of tanning material in the leather.

The one-inch square samples were tested for abrasion resistance through the kind cooperation of the British Boot, Shoe and Allied Trades Research Association, Kettering, England. The test consists in abrading two specimens with abrasive cloth, one from the grain side and one from the flesh side, until both are worn half way through. The rate of abrasion is expressed in millimeters of thickness abraded per 1000 machine cycles.

The physical test results are summarized in Table IV. Results on a sample of commercial sole leather are included for comparison.

TABLE IV

Physical Tests (Mean Values)

Tannage No.	Per cent condensate	Per cent quebracho	Thickness yield, %	Apparent density, g./cc.	Water absorption, %	Water solubles, %	Stitch Tear Strength, lb./in.	Rate of Abrasion mm./1000cycles
1	100	0	129	0.887	52.5	0.1	1220	3.6
2	75	25	147	.909	45.5	0.3	1200	3.7
3	50	50	144	.920	44.7	0.5	1190	4.0
4	25	75	147	.926	43.3	0.7	1170	3.8
5	0	100	146	.934	43.0	1.0	1170	4.1
Commercial–sample		—	—	1.012	51.0	18.8	820	5.2

Discussion of Results

Statistical analysis of variance showed that in most cases, the mean values for the various physical tests were not significantly different. However, there are clear-cut trends in many of the properties in Table IV. As the proportion of condensate in the blend increases and the proportion of quebracho decreases, the apparent density of the leather decreases; the water absorption increases, and the stitch tear strength increases. The abrasion results do not show as distinct a trend, but a lower rate of abrasion is indicated for the blends rich in condensate. In the case of thickness yield, any blend containing over 25 per cent of quebracho appears to give the same result as quebracho alone.

Most of these physical characteristics appear to be connected with the amount of tanning material in the leather. This value was expressed as weight yield in Table II. As increasing amounts of condensate are blended with quebracho, the weight yield of the leather decreases. The leather contains a smaller proportion of tanning material and a larger proportion of fibres. This result in higher stitch tear strength and abrasion resistance. There is also a higher proportion of voids, as shown by the lower apparent density and higher water absorption. Curling due to treatment with perspiration increases, since there is less tanning material in the leather to prevent it, but there is little shrinkage due to perspiration, showing a good resistance to detannage.

Most of the undesirable features could probably be corrected by building up the weight yield with concentrated liquors. For example, the leather tanned with the 50–50 blend as described had a satisfactory degree of tannage but a low weight yield. Following the vat tannage the leather could be drummed with enough concentrated 50–50 blend to build up its weight yield and obtain a leather similar to leather tanned with straight quebracho.

Summary

Five mixtures of quebracho and the phenol condensate of a decalcified ligninsulfonate material were evaluated by tanning pieces of heavy hide. The mixtures ranged from 0 to 100 per cent condensate. From the methoxyl contents of the resulting leathers it was shown that relative uptake of condensate and quebracho from a 25 per cent condensate mixture was approximately the same as their proportion in the liquor, but for mixtures richer in condensate the uptake of quebracho was greater than its proportion in the liquor. It was found that the highest leather yield value (on a weight basis) was given by quebracho alone, but the highest degree of tannage was given by a 1: 1 mixture of quebracho and condensate. Going from 0 to 75 per cent condensate, the thickness yield of the leather was unaffected; apparent density was reduced; water absorption was increased; perspiration resistance was slightly reduced, and abrasion resistance was slightly enhanced. The leather tanned with condensate alone was unsatifactory in weight and thickness yield. The properties of the leather tanned with the condensate, either alone or blended with quebracho, showed that the tannage was stable and that its stability complemented that of quebracho tannage, although the actual amount of tanning material in the leather was smaller. The properties of the leather tanned with the 1: 1 mixture of condensate and quebracho were close enough to quebracho-tanned leather to justify further evaluation of this blend as a heavy-leather tanning material.

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Discussion

Mr. Ira D. Clarke (Agricultural Research Service, U.S.D.A.): I think we all have found this a very interesting paper and the preliminary results show that the evaluations warrant some further study on a larger scale.

I would like to ask: were these leathers rolled before evaluation? I understood you to say that the leather was as firm or firmer than the commercial leather?

Mr. Kenzie: That is correct. And the leathers were compressed in a Carver press.

Mr. Clarke: There was more or less comparable pressure on the various leathers so that they would only be slightly firmer?

Mr. Kenzie: The difference in firmness was quite appreciable. That probably was a characteristic commercial leather we had on hand. As you know, there is a great deal of variation in commercial leathers as to firmness.

Mr. Clarke: I have not had much experience with ligno-sulfonates. Are there any questions from the floor?

Dr. J. R. Salvesen (Marathon Corporation): We have done some work on ligno-sulfonates in the past, as some of you may know. We have not gone to this interesting study of finding out what would happen if we condensed the ligno-sulfonate. This has not been done for various reasons.

In the first place we have felt that the ligno-sulfonate molecule is rather big as it is and it would be going in the wrong direction to make it still bigger.

The other, of course, is the economic question involved. I would like to ask the speaker if he has made a comparison between straight ligno-sulfonate without condensation and with phenolic condensed lignin. How big a difference is there? Some of the effects you have given in your tables here are fairly well known as resulting from ligno-sulfonates as such, without the condensation with phenol, such as the solubilizing effects, and decrease in solubles. Those are effects which are pretty well known with the straight ligno-sulfonates. Is there any way this has been enhanced by condensation with phenol?

MR. KENZIE: Yes, we have run previous experiments comparing the original ligno-sulfonates with the condensation product and we have found that the condensate gives a higher degree of tannage, that it raises the shrinkage temperature of the hide very appreciably and it protects the hide from tryptic hydrolysis.

Those are three examples of the differences. And those have indicated to us that we have achieved a considerable improvement over the starting material.

DR. SALVESEN: I do not want to monopolize the floor on this. We can continue our discussion. But I would want to bring out this point: that in this very interesting work you have used vegetable tans, as another component in the tannage. When you do that you take care of the shrinkage temperature without having to add phenol as a condensation product.

In other words, my question is, what would be the difference in analysis and in properties if you used the straight ligno-sulfonate along with quebracho in the same proportion as you did for the condensation product?

MR. KENZIE: I did not present any actual figures to illustrate the effects of the condensate in preference to ligno-sulfonate in the case of blends, but I think we could fairly assume that the condensate would give, in blend with quebracho, a higher yield, and that it probably would give a better resistance to tryptic hydrolysis than the ligno-sulfonate.

MR. J. D. TOLLIDAY (Victoria, Australia): If I understood the speaker correctly, he made the various strength liquors he used by making up a concentrated solution and diluting with water?

MR. KENZIE: Right.

MR. TOLLIDAY: That gives you nontannin concentrations completely different than one obtains in normal practice. Don't you think that the nontannins play such an important role in vegetable tanning that one should exercise some caution in interpreting results obtained under conditions so different? Don't you think that your physical properties and your comparisons could be quite different where you had nontannin concentrations similar to what would be obtained in practice?

The point is that really under this method of investigation you have very largely ignored the influence of nontannins in the vegetable tanning processes.

MR. KENZIE: Perhaps you could tell me some other method?

MR. TOLLIDAY: The only other method I know is the method of preparing a rocker set.

MR. KENZIE: I am sorry, I did not understand you. We have done that as a subsequent experiment. This was more or less of a preliminary, and as you

can imagine, it would have been prohibitively complicated to try to set up different rocker systems in a laboratory, but we have subsequently set up a rocker system using the fifty-fifty blend and we have got the full effect of variations in purity as well as tannin content, pH, and so on.

MR. TOLLIDAY: Were there essential differences in the results?

MR. KENZIE: Yes. We found that the rate of tanning is slowed up appreciably when we used this particular condensation product. This is just one of the headaches we have run into in this particular line of development and we have found that this ties in with something Dr. Salvesen said, too.

We found that the governing factor is the molecular weight and we have to go to a very low molecular weight material to condense with the phenol in order to get a rapid uptake of tannin from the rocker system.

MR. CLARKE: Mr. Filachione.

DR. FILACHIONE: I have no additional comments to make. I want to congratulate the authors on their work. I think sulphite waste liquor will always be an intriguing material for utilization in many applications.

MR. E. FACER, Jr., (U.S. Testing Company): We did experimental work in blending ligninsulfonate with quebracho and we found, by analyzing the waste liquors, that ligninsulfonate gives us a better pickup of the tannin, by having it in the blend, than a straight quebracho. Maybe the speaker can explain this.

MR. KENZIE: I could not explain it. That sounds as though it is quite at variance with what we obtained on our material. There are big variations from one material to the other, of course, and that might explain it.

MR. ROSS DONOVAN (Collis Leather Co.): You said you did not see too much significance in these results. Could you do some of the hysteresis tests of Dr. Roddy with greater significance?

MR. KENZIE: That would be a good idea in a later experiment. At the present time we have used up all of our experimental material.

Note on "An Electrographic Study of Chromium Sulfate Complex Ions".

By S. G. SHUTTLEWORTH

In a recent paper[1] Gustavson has selected results of several workers using exchange resin techniques to show that there is quite good agreement in the

determination of the proportion of cationic and non cationic complexes of basic chromium sulphate solutions. What he has omitted to point out is that none of these selected results is in conflict with the writer's electrographic data [2]. The electrographic results show clearly that the cationic character is reduced by sulphate additions and the findings are supported by analytical and spectrophotometric data as well as by mass action considerations. The reliability of the methods is established by the behaviour of complexes of known structure.

Gustavson's position that the presence of H ions converts an anionic or non cationic chromium complex to the cationic form in a period of 10 to 15 minutes at room temperature appears to be untenable, as the writer has proved [3] that H ions react extremely slowly with chromium complexes at room temperature. On the other hand the processes of hydrolysis and olation are very rapid. Therefore, in applying Gustavson's exchange resin techniques, the manifold dilution involved in starting with concentrated solutions must cause considerable hydrolysis and olation in the absence of excess H ions to counteract this. If, in the time period of the exchange resin technique, this hydrolysis and olation is not accompanied by an equivalent release of sulphate ions from the complex, the result will be the artificial production of non ionic and even anionic complexes. This applies to all techniques involving a dilution factor. The exchange resin technique is subject to the further weaknesses that enlarged complexes may be unable to penetrate the resin, and that the dilution caused by the water content of the resin may cause olation and complex enlargement inside the resin network, with some resulting fixation.

A striking example of misleading results that may be obtained by the exchange resin technique is Gustavson's finding [4] that a solution having the overall composition $Cr_4(OH)_9Cl_3$ + 7 Na Cl (1 g. – equiv. Cr per 1.), aged 4 weeks, contains 28 per cent cationic and 72 per cent non-ionic chrome complexes. Both the writer [5] and Kuntzel, Erdmann, Spahrkas, and Van Thaden [6] have shown by conductimetric studies that chloride ions do not co-ordinate appreciably to chromium except at very low basicities, not at all at basicities of 33 per cent and higher. This finding was confirmed by the above workers by electrophoretic measurements.

Disagreement with Gustavson is mainly related to his emphasis on the presence of marked proportions of anionic complexes in freshly boiled commercial chromium sulfate tanning solutions, and his theory that a change in charge *as such* affects the extent of co-ordination of the chromium to the protein carboxyl groups. For example a sucrose reduced bichromate liquor freshly boiled at 1 gm. eq. Cr/1 was found by him [1] to contain 65 per cent cationic, 21 per cent non ionic and 14 per cent anionic complex which changed on ageing to 93 per cent cationic and 7 per cent non ionic complexes. The former result is in conflict with the writer's electrographic result [2], and comparisons

between chrome uptake of the two liquors by hide powder showed no difference.

The probability of the co-existence of anionic, non ionic and cationic complexes in a basic chromium sulphate solution at equilibrium would appear to be bound up with simple mass action principles which take account of the competition between water molecules and sulphate ions for the available co-ordination position of the chromium. The writer has determined the stepwise stability constants for the various basic chromium sulfate complexes [8], and has shown that the addition of sulfate ions to convert a 33 per cent basic complex from an average of 2 positive charges per Cr. to an average of 1 positive charge per Cr takes place about a hundred times more readily than the conversion from 1 positive charge per Cr to an uncharged complex, followed by a similar reduction in order of probability in converting from an uncharged complex to an anionic complex. A stepwise drop in co-ordination stability is normal for chromium complexes [9, 10] but has been shown by the writer to be exceptionally steep in the case of basic chromium sulfate complexes because of the limited stereochemical possibility of six membered ring formation. It follows from this steep stepwise gradient of stability constants that the existence of appreciable quantities of anionic basic chromium sulf·te complexes is highly improbable except under conditions of extreme predominance of sulfate concentration compared with water concentration, such as during dehydration of chromium salts. Even less probable is the co-existence at equilibrium at the boil of 65 per cent cationic, 21 per cent non ionic and 14 per cent anionic complex.

Summary

The elextrographic results obtained by the writer [2] are shown to be well supported by other data and by theoretical considerations. It is shown that erroneous results can be produced by hydrolysis and rapid olation in the absence of excess H ions, which react extremely slowly with the chromium complex. Some conclusions drawn by Gustavson [4, 7] from exchange resin results are shown to be erroneous.

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ABSTRACTS

Practical Performance of Water-Conditioning Gadgets. By B. Q. Welder and E. P. Partridge. *Ind. and Eng. Chem.*, **46,** No. 5, 954 (1954). Observations are made concerning the practical performance of various gadgets in actual plant operation. Gadgets are defined as special devices requiring substantially no technical control, which are alleged to treat water by nonchemical means to prevent scale, corrosion and other troubles encountered in the industrial use of water. They are discussed in two categories, those with an external electrical circuit and those without such a circuit. The authors conclude that such devices usually do not prevent scale and corrosion under the varied conditions met in practice. R.H.T.

Analysis of Water-Formed Deposits. By F. U. Neat and A. A. Berk. *Ind. and Eng. Chem.*, **46,** No. 5, 961 (1954). The composition of water-formed deposits frequently can be interpreted to provide a guide for practical preventive or corrective treatment, either of the water or of its environment, thereby averting operating trouble or costly shutdowns. Complete and detailed information may show how to avoid repetition of difficulties; but, unless the information is accurate it may be misleading. Tried and tested methods of analysis are desirable and samples must be selected with care. Methods are given for moisture, loss on ignition, water soluble matter, sulfide sulfur, carbonates as CO_2, manganese, tin, sodium and potassium, silica, sulfur trioxide, copper and lead, phosphorous, iron oxide, titanium oxide, nickel oxide, zinc oxide, barium, calcium and magnesium. A diagrammatic outline of the procedure is given to make easy the elimination of unnecessary or undesired steps. Alternate methods are given where unusual apparatus or chemicals are required. Results of analyses are often difficult to explain, and may be interpreted in various ways. R.H.T.

Scheme for Analysis of Industrial Water. By J. H. Phillips and K. G. Stoffer. *Ind. and Chem.*, **46,** No. 5, 970 (1954). This is essentially the report of a task group appointed to set up to develop a scheme for analysis of industrial water for the ASTM. It includes a comprehensive list of the properties and constituents of industrial water for which analyses are made. The mechanics of arranging the analytical methods in a logical order proved to be the most difficult part of the problem. The scheme arranges the samples into samples for constituents affected by air content and subdivides these into flow samples and separate samples. Then samples for constitutents unaffected by air content are subdivided into separate portions of a single sample and separate samples. A system of lines and sample group blocks is employed to associate properties and constituents with their appropriate sample groups and to indicate possible successive analyses of several constituents from a preceding analysis. The scheme brings together, in a manageable outline form, the methods for determining the many properties and constituents of industrial water. R.H.T.

Significance and Application of Water Analysis Data. By R. C. Ulmer. *Ind. & Eng. Chem.*, **46,** No. 5, 975 (1954). Many plants encounter water problems because of improper interpretation and use of analyses. Analyses of make-up water are concerned with determining its purity and detecting possible corrosion factors by tests for pH, carbon dioxide, and electrical conductivity. In the feed water system corrosion and deposits are the chief problems and analyses for pH, carbon dioxide and pertinent ions are conducted. In the boiler most attention is directed to scale, sludge, corrosion, carry-over and embrittlement. Analyses are made to investigate and control each of these. In steam and condensate analy-

sis, interest is in purity and corrosion, with analyses directed along these lines. Water analyses alone may not be sufficient. Deposits and corrosion products should also be investigated. Regular analyses and correct interpretation are recommended to ensure proper conditions in steam generating systems. R.H.T.

Significance of Boiler Deposit Analysis. By F. E. Clarke and R. D. Hopkins. *Ind. & Eng. Chem.*, **46,** No. 5, 979 (1954). Water-formed deposits are common causes of overheat failure in boiler tubes. Solution of deposit problems requires accurate analysis and proper interpretation of the data. The simplest deposits may be difficult to analyze, and complex boiler deposits, such as residues of fuel oil, lubricants or rust preventive compounds, frequently must be extracted and identified. Precipitation of barium and tin compounds with silica, or phosphate compounds with iron, can paint imaginary pictures of deposits that never existed. Examination of microstructure is an important step, as sources and structures of deposits can vary markedly, even though their chemical compositions are almost identical. The wise operator will consult the analyst to determine the nature of all boiler deposit. While a complete analysis may not be necessary in all cases, the wise analyst will equip himself with a scheme sufficiently comprehensive to cover all needs. The analytical scheme should be versatile enough to cope with the most difficult cases, yet flexible enough to handle the simple cases efficiently. R.H.T.

Internal Cleaning of Boilers. By J. M. Maloney. *Ind. & Eng. Chem.*, **46,** No. 5, 983, (1954). The basic solvent is 5 per cent HCl. In general cleaning is done in four steps. (1). Sufficient inhibited acid solvent is added to the boiler through a lower boiler connection and the proper acid strength and temperature maintained. (2). The chemical solvent remains in the unit from 6 to 8 hours. This is termed the "soaking period." (3). The boiler is drained and sufficiently rinsed with clear water. (4). Finally metal surfaces are neutralized by means of a 3 to 4 hour boil with alkaline solution. If there is much silica or complex silicate in the scale, some HF may be necessary. Organic matter may require special treatment. Preliminary boiling out with oxidizing alkaline solution has served well where high ignition loss indicates organic matter. Newly developed inhibitors are said to be stable up to 190°F. These improve corrosion prevention during acid treatment but no inhibitor yet developed entirely prevents corrosion during this treatment. However such attack is usually inconsequential. Auxilliary boiler drains, after-rusting, and chemical cleaning of new boilers are discussed briefly. R.H.T.

Preparation of Feed Water Make-up. By S. B. Applebaum. *Ind. & Eng. Chem.*, **46,** No. 5, 985 (1954). New ion exchange water treatments introduced during the last few years are: (1) Silica removal demineralizing. (2) Hot lime zeolite. (3) Salt splitting by anion exchange following sodium zeolite: this reduces alkalinity or silica without demineralizing. Residual silica, as determined by three prevailing methods in parts per million, is as follows. Cold process pricipitate 2 to 3. Hot lime zeolite 0.5 to 1.0. Demineralizing 0.05 to 0.2. All three are described and discussed. R.H.T.

The Synthesis of Amphoteric Tanning Materials. I. By K. Rosenbusch. *Das Leder*, **6,** 58 (1955). The object of the present work was to make synthetic tanning materials that would not be dependent on a sulfo group for solubility, but would be made soluble by the hydrophilic property of salts of quaternary bases. Such substances, if based on phenolic materials, must have amphoteric properties. Basic groups should give the desired solubility without lowering tanning ability. Introducing a basic group directly in the ring of phenol-novolak would involve nitration and reduction of the nitro group to an amino group and this would be too costly. Introduction of an amino group in a side chain by the Mannich

reaction was therefore investigated. In this reaction an amine, formaldehyde and a third component are coupled by formation of both C-C and a C-N bond; for example accetone, formaldehyde and an amine are condensed as follows:

$$CH_3—CO—CH_3 + HCHO + RNH_2 \cdot HCl = CH_3—CO—CH_2—CH_2—NHR \cdot HCl + H_2O$$

The two components must have nearly the same reactivity with formaldehyde or only one may react. Condensation in boiling aqueous solution of naphthol, aniline hydrochloride and formaldehyde produced yellow needles melting at 201° identified as 2,2—dihydroxy–dinaphthyl–(1)–methane. This compound with acetic anhydride gave bis–(2–acetoxy–naphthyl)–methane and on boiling lost 2 molecules of water to form 1,2,7,8 dibenzoxanthene, (dinaphthopyran). In the above condensation the aniline did not react because in aqueous solution the H atom in the alpha position of the naphthol is much more reactive than the H atom on the N atom of aniline in the salt form. When condensation was conducted in alcoholic solution and aniline substituted for its hydrochloride, the expected 1–anilino–methyl–2–naphthol was obtained in 95 percent yield. It melted at 131° and had the elementary composition $C_{17}H_{15}ON$. It, however, was insoluble in alkali suggesting a blocked phenolic group and the composition N–naphthyloxymethol aniline, but this was disproved by the fact that high pressure hydrogenation (Raney nickle, 250 atmospheres, 175°) produced 1–methyl–2–hydroxynaphthalene. If heated above its melting point, the white needles of 1–anilinomethyl–2–napthol changed to a brown, solid (on cooling) resin, insoluble in acid or alkali but soluble in organic solvents. This resin, when distilled in vaccuum at about 160°, decomposed to aniline and beta naphthol and at 305° changed to benzoacridine. Condensation of symmetrical xylenol with aniline and formaldehyde was attempted because the H atoms are more reactive than those of phenol, but less than that of the alpha hydrogen of beta naphthol. In aqueous solution a vermillion red resin was obtained that was insoluble in organic solvents or acid. When treated with hydrochloric acid and nitrate the resin gave an ether soluble, yellow nitrosamine derivative showing that there had been a true Mannich condensation. In alcoholic solution there were quantative yields of the mono-, di-, or tribenzylamine derivatives depending on the molar proportions of the starting materials. The mono derivative formed white needles melting at 124° and was shown to be the ortho compound by hydrogenation (catalytic) with formation of isopseudocumenol. The di- and tri- derivatives were thick, yellow oils, slightly soluble in dilute acid and alkali, and which split off analine on distillation in a vacuum. Catalytic hydrogenation gave a mixture of products in addition to the expected tetra- and pentamethylphenols. A new method for preparing tetramethylphenols is to condense isopseudocumenol, aniline and formaldehyde, then to split the product by hydrogenation with a nickel catalyst for 6 hours at 175° and 150 atmospheres pressure. Condensation of phenol and aniline resulted in a mixture of N-phenoxy-methylaniline and 2-hydoxybenzylaniline which could be separated with ether and alkali. The former was a brownish, acid-soluble oil (not pure) that changed on vacuum distillation to aniline and a yellow, alkali-insoluble resin. The 2-hydroxybenzylaniline was soluble in both dilute acid and alkali, gave a characteristic precipitation on neutralization but had a molecular weight that was too low for a tanning material. When heated above its melting point, it changed to a solid, yellow resin soluble in alkali, but not in acid. When phenolnovolak, made by condensing phenol and formaldehyde, was further condensed by heating for several hours in alcoholic solution with aniline and paraformaldehyde a yellow resin separated on cooling. This resin could be dissolved in alkali but not in acid. The preceding work showed that resins with the desired solubility properties could not be obtained by the Mannich condensation of aniline with monohydric phenols. On the other hand, such compounds were easily obtained with polyhydric phenols. Condensing equimolar proportions of resorcin, aniline hydrochloride, and formaldehyde produced a red amphotan that was soluble in water and gave a heavy precipitate with gelatin. This tannin was precipitated at its isoelectric point when alkali was added. The precipitate dissolved on addition of either alkali or acid as the

phenolate or salt of a quaternary ammonium base resp. The insoluble resin (from neutral solution) was difficultly soluble in ether but easily soluble in semipolar solvents, such as methanol, ethanol, diacetonealcohol, acetone, etc. It was readily salted out of acid solution as a lustrous, golden, creamy resin that was greenish brown when dry. Elementary analysis indicated the formula $C_{28}H_{28}O_5N_2Cl_2$. Lieberman's nitrosamine reaction was positive showing the presence of a secondary amino group. A primary amino group was also present which was formed by a Frieschen shift. Diazotization formed an azo component which condensed to an inner azo dye. During drying of the amphotannin some of the basic component split off and the remaining phenolic component condensed to a higher molecular, nitrogen-poor phenoplast. Neutralization of the resorcin-amphotan, having the formula $C_{28}H_{28}O_5N_2$·2HCl, caused precipitation of a phenoplast having the formula $C_{28}H_{26}O_{11}N$; that is, 5 benzene rings per nitrogen atom instead of 2. Similar amphotannins can be made with other polyhydric phenols, especially pyrocatechol and pyrogallol but not withphloroglucinol. During condensation with pyrocatechol an intermediate very stable addition compound of pyrocatechol and aniline hydrochloride could be isolated. This compound, $C_{12}H_{14}O_2NCl$., melted at 130°, could be distilled at 232-4° without decomposition but could be separated into its components by treatment with ether and alkali. I.D.C.

The Synthesis of Amphoteric Tanning Materials. II and III. By K. Rosenbusch. *Das Leder* **6**, 80 (1955). Because aromatic amines (as shown in part I) were not basic enough to condense to amphotans with monohydric phenols in acid solutions, an attempt was made to condense aliphatic amines, which are more basic, with phenols. Here also in aqueous solution monohydric phenols formed insoluble phenoplasts but polyhydric phenols condensed to amphotans. In methanol, equimolar proportions of phenol, dimethylamine and paraformaldehyde condensed quantitatively to an oil that was soluble in acid, but almost insoluble in alkali. The oil was separated by ether-alkali extraction into two fractions. The main portion, the alkali insoluble fraction, distilled under 15 mm. pressure at 105-106° without decomposition and formed a picrate melting at 151°. Catalytic hydrogen of the alkali insoluble fraction gave a quantitative yield of 1-methyl-cyclohexanol-(2); and formation of 3,5-dinitrobenzoyl-1-methyl-cyclohexanol-(2) from the latter the insoluble product was identified as 2-hydroxy-N-dimethyl-benzylamine and not dimethyl-phenoxy-methylamine. It was not a tanning agent because the molecule was too small. Condensing phenolnovolak with formaldehyde and dimethylamine in methyl alcohol produced an amphotan that was soluble in dilute acid and alkali and precipitated at the isoelectric point. It did not precipitate gelatine in the acid form, but did as the quartenary ammonium base form. Its nitrogen content of 9% showed that one dimethylamine group had coupled with each phenolic group. Dimethylamine is too expensive to use in making syntans, so the cheap ethanolamines were tested. Phenolnovolak condensed with monoethanolamine to a yellow, alcohol insoluble resin; diethanolamine to an alcohol souble resin that readily dissolved in acid and alkali. Hydrogenation produced a p-cresolnovolak type resin. By the above type of condensation, polyhydric phenols change to amphotans in aqueous solution. Intermediate products could be separated. With ethanolamine the oxazolidine described by Paquin (*Chem. Ber.* **82**, 316) was found. With diethanolamine 3-beta-hydroxyethyl-oxazolidine was obtained. This compound distilled under 31 mm. pressure at 128° without decomposition. It condensed with resorcinol to N,N-bis (beta hydroxyethyl)-2,4-dihydroxbenzylamine and with pyrogallol to N,N-bis (betahydroxyethyl)-3,4,5- trihydroxybenzylamine. These crystalline Mannich bases showed the typical behavior of amphotans. On adding alkali to the hydrochloride solution a precipitate formed which could be dissolved in either acid or alkali. If the precipitate was filtered off and analyzed, the nitrogen content was near that of a polyhydroxynovolak and there was only one basic group condensed with 4 resorcinol groups instead of 4. Inorganic bases could also be used, resorcinol, ammonium chloride and formaldehyde con-

densed to a tannin that penetrated rapidly because of its small molecule and, for example, was useful in correcting case hardening in vegetable tanning. Condensation could also be obtained by fusion. If the Mannich condensation of monohydric phenols, aldehydes and hydrochlorides of amines, was done by fusion, soluble products were obtained, whereas in aqueous solution the products were insoluble. Symmetrical xylenol, formaldehyde and ethanolamine gave the mono-, di-, or tri- benzylamine derivative depending on the amount of amine used. Phenolnovolak, ethanolamine and paraformaldehyde by fusion produced a synthetic amphotan similar to that made in alcoholic solution. Polyhydric phenols can be used, also the amine salts instead of the free base, provided no free acid is present. The most important tanning field for the Mannich condensation lies in the possibility of changing vegetable tannins to amphotannins. Experiments along this line were reported previously by Küntzel and Rosenbusch (see *this Jour.* **50,** 60). Typical formulae are given. The use of amphotannins has been described by Mauthe and Faber (see *this Jour.* **48,** 693). I.D.C.

Progress in the Leather Field. By G. Mauthe. *Das Leder,* **6,** 49 (1955). The revolutionary changes in the leather industry in the nineteenth and first part of the twentieth centuries are no doubt tied to the industrial revolution. Two factors are of importance in the development of the leather industry: (1) the nature of collagen and the possible countless modifications of it by tanning; (2) the nature and size of the market. The fact that animal hide can be changed by technical processes into the most varied types of products, all called leather, makes it probable that the future holds a place for medium sized firms which make special articles of high quality, but small firms must adopt all improvements. For sole leather the standards of quality have been based on analysis, strength and water resistance. The question of old versus modern method of tanning has never been settled. It is not yet possible to predict the effect of a modification in tanning procedure on the wear or water resistance of sole leather. Because of the competition from synthetics. re-tannage with chrome or vegetable-syntans is being studied intensively. Impregnation with monomers and polymerization in the leather has been abandoned in Germany, because it is very difficult to polymerize in wet leather. Impregnation of emulsions of high polymers is also difficult. Silicone treatment of sole leather may not be effective. The mechanism of waterproofing is not clear, but swelling of the leather fibers by water must not be interfered with; coating them with a waterproofing agent might result in more rather than less water being pumped through the leather. A fundamentally improved leather probably will be by a new process. The study in England of the acid-salt balance in vegetable tannins may lead to better vegetable leather. Tanning in an organic solvent requires all new equipment and is suitable only for very large scale plants. The insole problem is one of deterioration (detannization) of leather by alkali from sweat or bacteria-decomposed sweat. The remedy is either to treat the leather with a harmless acid to resist the alkali or to modify the vegetable tannin so it will not be dissolved. Technically the insole problem can be considered solved. Upper leather quality has been improved by the use of masked chrome salts. Criteria of quality are hand, tightness and fineness of grain, uniformity of coating, fastness to wet and dry rub, cutting value, etc. In Europe chrome content is considered of great importance, whereas in the U.S.A. chrome content is lower and the desired uniformity and cutting value are obtained by retannage with special vegetable extracts or syntans and fatiliquoring. Resin tannages are used for filling. Many new types of finishes are now used. They should be fast to acetone, cold, dry-hot rubbing and to ironing. Polymer emulsions are thermoplastic and therefore not stable to hot ironing or acetone. Astonishing attention is given to finishing in the U.S.A. I.D.C.

Comments on the Article "Progress in the Leather Field". by G. Mauthe. By U. Rahde. *Das Leder,* **6,** 133 (1955). (see preceding abstract). The statement that it is not

possible to get a plastic finish that is fast to acetone, hot rubbing and hot ironing is not correct. Such a finish is made by Kasika, Chemische Fabrik GmbH, Berlin- Britz.

I.D.C.

Oxidimetric Determination of Synthetic and Vegetable Tannins in the Presence of Each Other. By E. Békés. *Das Leder*, **6**, 97 (1955). A method has been developed by which the proportion of vegetable and synthetic tanning materials can be determined with sufficient accuracy for calculation of the tannin balance. It is based on the Loewenthal method. Vegetable tannins require several times as much permanganate as sulfite waste liquors. Since the major portion of a synthetic tannin is based on sulfite waste liquor, the new method became possible. The classical Loewenthal method, however, is not sufficiently accurate. The permanganate consumption is influenced by the following factors: Inexact determination of the end point; (2) concentration of permanganate and the rate of addition; (3) temperature; (4) tannin content of the solution to be analyzed; (5) concentration of the indigo-carmine solution; (6) degree of acidification of the tannin solution with sulfuric acid; (7) standardization of the permanganate solution. Intensive study of each factor resulted in the following conclusions: 1. The end point observed with the naked eye may vary by from 15 to 20 percent depending on lighting conditions (bright or cloudy day, artificial light, etc.). The indigo-carmine color change is not sharp and the permanganate color is not present until much more permanganate has been added. The Pulfrich-Photometer was therefore adopted for determining the end point. It was used with light filter S57 which transmits yellow. The titration curves (volume of permanganate versus extinction coefficient) for quebracho, "Lignotan" and indigo-carmine reached end points at extinctions between 0.1 and 0.25. The end point 0.3 was therefore chosen. It was reproducible to 0.1-0.5 ml. even with syntans which required only a little permanganate and remained constant for 2 hours. 2. As a drop of the potassium permanganate solution is added there is a local high concentration of permanganate that will oxidize some of the components that are more difficult to oxidize than indigo-carmine. The reduction potentials of the individual components are all close together. A syntan solution containing 4 grams tannin per liter was titrated with $N/20$, $N/40$ and $N/60$ permanganate, and the results showed 4.6, 4.0 and 3.2 grams tannin resp. A higher concentration of permanganate causes a more intense oxidation and a greater consumption of permanganate. When 20 ml. of permanganate was added at once and then the titration was completed dropwise, 5 percent more premanganate was used for a quebracho sample and 19% more for a lignotan sample, than when all the permanganate was added dropwise. To obtain a reproductible drop rate, the burette stopcock was modified so it could always be opened to the same degree. 3. On the average, 17 percent more permanganate was used at 40° than at 20°. This means that 0.15 ml. more permanganate is consumed per degree rise in temperature. 4. With increasing concentration of the tannin solution the permanganate consumption increased 3 or 4 percent. 5. An increase of the amount of indigo-carmine added to the tannin solution increased the permanganate consumption although the consumption of a pure indigo-carmine solution was independent of temperature, acidity, rate of addition of permanganate and concentration. The permanganate consumption for 0.1 gram of indigo-carmine was exactly half that for 0.2 gram. 6. The permanganate consumption with 10 ml. of concentrated sulfuric acid was 16.49 ml. and with 100 ml. of acid was 15.18 ml. In strong acid the tannin is more easily oxidized. 7. Oxalic acid was used for standardization of the permanganate solution because variations of 8-10 precent were found in various gallic acid samples. The titration should be made as follows: Adjust the stopcock setting so the burette will discharge 50 ml. in $5 \mp .1$ minutes. Twenty-five ml. of the indigo-carmine solution, containing 4.0 grams of indigo-carmine and 25 ml. of concentrated sulfuric acid per liter, when titrated in 750 ml. of water should consume 21.9-22.1 ml. of permanganate solution. Add 25 ml. of indigo-carmine solution

and 5 ml. of the tannin solution to be analyzed to 750 ml. of water in a flat porcelain dish 20 cm. in diameter. Stir vigorously (with a motor running at 60 r.p.m., and a stirrer blade 10 cm. long) while adding permanganate solution and determine the end point at an extinction of 0.3 with a photoelectric colorimeter (filter S57). Extinction measurements are made by removing solution to a 5 ml. cell then returning it after the measurement. Plot the results at 0.5 ml. intervals to locate the 0.3 extinction point. With practice only two measurements will be needed. Repeat the titration on 5 ml. of the tannin solution, after removing tannin with weakly chromed hide powder by the shake method. Determine tannin by difference. Each tanning material has a characteristic permanganate number, which is defined as the milliliters of $N/40$ permanganate solution consumed by the pure tannin in 5 ml. of tannin solution containing 4 grams tannin per liter. Values shown range from 0 to 17.4 In mixtures of one vegetable tannin and one syntan the proportion of syntan in the mixtures (x) can be found from the formula:

$$X = \frac{V-M}{V-S} \cdot 100$$

where V is the permanganate number of the vegetable tannin, S that of the syntan and M that of the mixture. This method can be applied to used tan liquors, because it was found that a drop in purity did not change the permanganate number. Analysis of spent liquors from a number of sole and upper leather tanneries showed that these liquors, which were mixtures of vegetable and synthetic tannins, always contained a relatively greater proportion of syntan, meaning that the syntan was taken up less readily by hide than vegetable tannin. Variations in pH, concentration and acidity modified tannin take up, but did not change the picture; the ratio of vegetable tannin to syntan was always shifted in favor of the latter. I.D.C.

The Extraction of Vegetable Tanning Materials for Tannin Analysis. Proposed Change in the ALCA-Extractor. By E. Gülbaran. *Das Leder*, **6**, 102 (1955). In the Koch extractor the material being extracted is constantly immersed in a relatively large float. The ALCA extractor is superior, because there is no float and most of the extractable matter is removed in the first stages of the extraction; this is called a differential extraction. The difference between results with the two extractors is greatest when small volumes of extract per given amount of material are collected and this difference decreases as the volume of extract is increased. In the Koch extractor the extract is kept at 100°C. for a long time compared to that in the ALCA extractor. In the ALCA extractor 86 percent of the total extract in a valonia sample came off in the first 100 ml. but only 33 percent in the Koch extractor. The latter requires constant attention, whereas the ALCA extractor does not. The disadvantages of the ALCA extractor are that the material must be stirred in a beaker with water at 95° and thoroughly moistened before it is put into the extractor. Also only one extraction temperature is possible, although it can be easily modified so that water at any desired temperature can be dropped onto the sample The diameter, 53 mm., is too great. The water drops on the middle of the charge and material toward the outside edges is progressively less efficiently extracted. This defect is the reason the German commission found no differences between the two extractors and decided to retain the Koch. The diameter was therefore reduced from 53 mm. to 35 mm. in the modified extractor which was assembled as follows: In the bottom was placed a perforated copper or brass disc, 32 mm. in diameter, covered with a patch of cotton of proper size, and held down by a rubber ring (37 mm. outside diameter, 30 mm. inside diameter) which fitted snugly against the wall of the extractor and prevented material from passing the edge of the brass plate. A layer of glass beads (3.5 mm. in diameter) was added, followed by the material to be extracted, another layer of glass beads and a perforated rubber plate (37 mm. in diameter,

5 mm. thick) with notched edges. The rubber plate was pressed down on the charge and because of its tight fit against the extractor wall prevented steam from pushing up the charge. An extractor was assembled from 2 pieces of glass tubing 35 mm. and 50 mm. resp. in diameter and separated by cork. Some data with the two extractors are given in the following table:

	Koch		ALCA Improved		
Material	Total solubles	Tannin	Total solubles	Tannin	Additional Tannin With ALCA
	%	%	%	%	%
Spruce bark	22.0	12.4	24.8	14.2	15
Bark of P. silvestris	6.2	2.7	9.7	4.5	67
Bark of P. brutia	17.8	10.2	21.2	12.2	20
Bark of P. pinea	21.9	16.0	24.4	17.6	10
Valonia	49.6	32.1	53.5	34.9	9
Myrobalans	60.4	37.7	61.3	38.8	2

At the end of the extraction, liquor from the Koch extractor almost always gave positive gelatin and iron tests, whereas that from the ALCA extractor gave negative tests.

I.D.C.

The Leather Industry in New Zealand. By E. Horn. *Das Leder*, **6,** 105 (1955). The tanneries tan sole, side, sheep lining, chamois, slipper and jacket leathers. They have chemical control, but unskilled labor. The leather is of good quality, but not equal to European leather. The sheep and lamb skins are equal to European skins but other skins are inferior as they have loose weave, grain defects, and a poor take-off. Many deerskins are exported, mostly to the U.S.A. Deer were introduced 70 years ago and are now a plague. Sheepskins are good, as they are from coarse-wooled sheep. Twelve million lamb, and 4 million pickled and 1 million dry sheepskins are exported annually. After pulling the wool, sheepskins are limed in a paddle, often bated, pickled in salt and sulfuric acid, fleshed, sorted, rolled in bundles of 6, and packed in wooden casks. The U.S.A. requires a high acid content in pickled skins, but based on work at the New Zealand research institute, some factories now reduce the amount of sulfuric acid and add beta-naphthol as a preservative. I.D.C.

Darmstadt Hide Powder. *Das Leder*, **6,** 109 (1955). The Darmstadt Institute for Tanning Chemistry will now supply both chromed and unchromed hide powder. The chromed powder is for tannin analysis by the official IVLIC, filter method. It will be prepared by the method described by Küntzel and Kurth (see *This Jour.* **50,** 213). I.D.C.

The Relation between the Thermal Conductivity of Fur Skins and Hair Density. By F. Brugger. *Das Leder*, **6,** 121 (1955). The best fur garments have the greatest insulating power. The measurement of heat conductivity is greatly influenced by the pressure on the specimen during measurement. As the pressure increases the thickness and the insulating power of the fur decrease. Thermal measurements were therefore made under a standard pressure of 1 kilogram per square decimeter. Thickness was also measured under this pressure by a special gage. The conductivity apparatus used was that described by Stather and Schöpel (See *This Jour.* **44,** 752). It consisted of a copper disk, 113 mm. in diameter (area 1 square decimeter,) supported on a wooden base and controlled to a temperature of 40°C by a heating coil, thermometer and relay. Supported on this disk

were, in order, a plexiglass disk of known thermal conductivity, another copper disk fitted with a thermometer, the fur specimen, and finally a metal chamber through which water at 20°C. was circulated and which was adjusted by a counterweight to exert a pressure of 1 kilogram on the specimen. The whole was insulated with felt. The conductivity, in kilocalories per square meter, per meter thickness, per hour, with a temperature differential of 1°C. was calculated from the formula:

$$L = K\, d_x \frac{40 - t_x}{t_x - 20}$$

where the constant, $K = L\rho/d\rho$ and d_x is the pelt thickness, $L\rho$ the conductivity and $d\rho$ the thickness of the plexiglass and t_x the temperature of the upper copper disk after it becomes constant (usually in about 4 hours). The insulating value is given by d/L. For rabbit fur L varied from 0.061 to 0.073 with an average of 0.068. For sheepskin L varied from 0.081 to 0.089, with an average of 0.082. Hair density (weight of hair per unit area of skin) was determined as follows: A 1x1 cm. square of leather was cut (from the flesh side to avoid cutting hairs), the hair was combed in one direction, a ruler 25 mm. wide was placed on the specimen with one edge coinciding exactly with one edge of the specimen, hairs extending beyond the opposite edge were cut off with a razor so that the remaining hair on one edge was 25 mm. long and on the opposite edge 15 mm. long. This operation was repeated on the other 3 sides of the specimen, after which the hair on the specimen formed a square shaft 15 mm. tall, and terminated in a pyramid with hairs 16.7 mm. long at the peak. The specimen was weighed before and after shaving off the hair, and the hair weight, in milligrams per square centimeter, (mg/cm^2) was determined by difference. By taking samples at regular intervals over a skin, it was found that one specimen taken half-way between neck and tail and half-way between backbone and belly edge gave average values for the skin. A number of raw skins were divided into 5 grades based on hair densities of 37, 32, 27, 22 and 17 mg/cm^2 resp. for the grades. After dressing, these furs were put into 4 grades based on densities of 30, 25, 20 and 15 mg/cm^2. These gradings were then compared with the average grades of 2 men who sorted the raw skins and those of 4 men who sorted the dressed skins. The maximum difference between graders was 2 grades. There was a difference between density grade and sorting grade, greater than one-half grade, for 14 raw and 4 dressed skins, so that sorting the finished skins was much better than sorting raw skins. The data show that the insulating value of a fur was proportional to its thickness measured under a pressure of 1 kilogram per square decimeter. The thermal conductivity measurement therefore can be replaced by a thickness measurement. The quality of a fur is determined primarily by the hair density and furs can be graded exactly on this basis. Hair density is proportional to the fur thickness measured under a pressure of 1 kilogram per square decimeter. I.D.C.

The Determination of Extractable Fat in Leather. (Report of the working group on Hides and Leather of the Swiss Association of Leather Chemists (VESLIC). By W. Weber. *Das Leder*, **6**, 127 (1955). The following data were obtained in 3 Swiss Laboratories by extracting with petroleum ether (boiling at 40°-80°C.), carbon tetrachloride (77°) and methylene chloride (37°-39°) in a Soxhlet extractor or in a rubber extraction apparatus (see Zimmerman and Pangborn; *This Jour.* **46**, 342). The group concludes that (1) ether extracts a little more fat than petroleum ether (average fat content of 5 leathers with petroleum ether, 22.90%, with ethyl ether 23.38%); (2) chlorinated hydrocarbons dissolve more fat from leather than petroleum ether; (3) methylene chloride is a better fat solvent than carbon tetrachloride or chloroform and is easy to use and not flammable; (4) Methylene chloride decomposes in direct sunlight or in artificial

Solvent		Fat content, duplicates and average								
		Upper leather %			Belting leather %			Chrome belting %		
Pet. ether	S	22.8	22.7	22.8	18.8	18.8	18.8	24.7	24.7	24.7
Carbon tet.	S	23.7	23.8	23.8	20.4	20.4	20.4	25.5	25.3	25.4
Methylene	S	23.5	23.8	23.6	20.7	20.8	20.8	25.0	25.0	25.0
Chloride	R	23.8	23.7	23.8	20.8	20.7	20.8	25.1	25.1	25.1

Note: S=Soxhlet, R=Rubber extractor. 30 solvent changes in S; 5 hours in R.

	Fat content with		
	Petroleum ether %	Carbon tetrachloride %	Methylene chloride %
Upper leather	11.2	12.1	15.6
Upper leather	12.7	13.2	15.7
Harness leather	21.0	22.1	24.6
Harness leather	23.0	24.1	26.2
Strap leather	6.0	6.7	7.5
Chrome leather	5.7	6.0	7.1
Chrome leather	8.7	9.3	10.6
Chrome leather	16.0	17.5	20.6

Note: Leathers oiled with partial use of synthetic products which condensed with time; extraction after aging 3 months.

ultraviolet light with liberation of hydrogen chloride, but the amount liberated is not great enough to affect the composition of the leather; (5) The composition (acid no., saponification no., drop point) of the fat extracted with chlorinated hydrocarbons was the same as that extracted with petroleum ether, except for a tendency toward a higher saponification number; (6) The rubber extraction apparatus was more troublesome to use and gave no better results than the Soxhlet extractor. On the basis of this work, the determination of fat in leather should be made in a Soxhlet extractor with methylene chloride.

I.D.C.

The Advantages of an Aluminum Retannage of Chrome Suede Leather. By G. Otto. *Das Leder*, **6**, 130 (1955). Eitel has stated (see *This Jour.* **50**, 327), that chrome leather after retannage with alum, has a gray tinge. The advantages of an alum retannage, which never introduces more than about 1 percent of aluminum oxide (Al_2O_3), is that the aluminum greatly increases the affinity of the leather for anionic dyes. The color is fuller, more saturated, more resistant to buffing and never grayer. It is important that the aluminum salt have a basicity greater than 60 percent, Schorlemmer. More of a black and of a brown dye were absorbed by precipitated aluminum hydroxide than by precipitated chromium hydroxide. Eitel also stated that alum retannage suede is greenish. Treating dyed leather with an alum tannage instead of acidifying it with formic acid is common practice. In dying with substantive dyes, with addition to ammonia, the affinity of the leather for dye is diminished to such a degree that an appreciable amount of dye remains in the bath. If the dye is then fixed with formic acid as usual, the sharp pH drop affects almost entirely the outermost layers of the leather and the dye is nearly all fixed on the

surface of the leather and is lost later during buffing. Fixing with basic aluminum chloride is much more favorable. It lowers the pH less violently for it gives up acid only as it hydrolyses. It therefore affects deep layers as well as the upper layers of the leather. Also the highly basic aluminum compound is fixed by the leather and in turn fixes some of the remaining dye in the bath. This results in an especially saturated color exactly in the zone which forms the leather surface after buffing. If cheaper dyes are used which change from greenish black to reddish black with a pH from 6 to 4, then unbuffed, alum retanned leather may appear greenish black in comparison with leather acidified with formic acid. However, after buffing alum retanned leather will be a deep, saturated black. I.D.C.

View on the Article "Serial Experiments on the Clarification of Waste Water from Leather Factories in Worms". By Depner and Germans. *Das Leder*, **6**, 133 (1955). For fish to survive, water must contain at least 4 milligrams of oxygen per liter and the biological oxygen demand must not exceed 5 milligrams per liter. To meet this requirement city sewage must be mixed with 3 to 4 times its volume of clear river water. The biological oxygen demand of tannery waste water is 1000 milligrams per liter and of city sewage, 300-500 milligrams. Addition of 10 percent of sewage to tannery waste water would give no improvement. Microorganisms could not remove chrome. Sediment would provide no nourishment for fish; they were probably feeding on Tubifex worms. *Reply by J. Schlichting.* After strong aeration, tannery waste water would support fish life only if sewage had been added. Lower organisms can remove substances poisonous to fish; they were shown to remove phenol from gas works waste water. The tannery waste in the settling basin contained nematodes and bacteria. I.D.C.

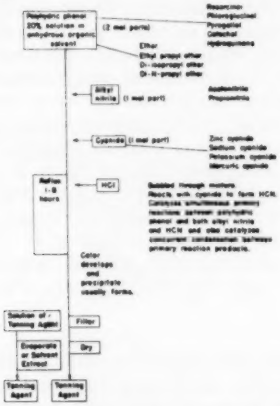
PATENTS

Method of Producing a Food Product From Scrap Particles of Hide. U. S. Pat. 2,676,168. David Torr, New York, N. Y. assigned to Charles J. Ely, Oakland, N. J. Apl. December 23, 1950. 1. The method of treating scrap particles of hide which comprises reducing the hide to a state of colloidal dispersion in a colloidizing operation, producing a product having the Brownian movement, the particles being less than 10 microns, the colloidizing operation being carried out at a temperature which hydrolyzes protein of the hide into gelatin.

Water-Soluble Derivatives of Unsulfonated Lignin. U. S. Pat. 2,676,170 George Harold Pattersen, Wilmington, Del., and Walter Jean Balon, Carneys Point, N. J. assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware. Apl. July 15, 1950. 3. The process of producing a water-soluble derivative of lignin, having tanning powers, which comprises reacting lignin, in alkaline solution and at a temperature between room temperature and 105° C., with formaldehyde and a halogenoaliphatic carboxylic acid, and acidifying the reaction mass to precipitate the reaction product.

Process of Making Tanninlike Materials and the Resulting Products. U. S. Pat. 2,676,980. Shutung Tu, Racine, Wis., assignor to Tanexco, Inc., a corporation of Delaware. Apl. January 31, 1950. 1. The method of converting vegetable materials bearing materials capable of conversion to tannin-like material having the property of re-acting with animal skins to form leather, which comprises: extracting the vegetable material with an aqueous solution containing an amount of alkali sufficient to produce an extract having a pH of about 6.0 to 8.5 and then adding an amount of sulfur dioxide sufficient to reduce the pH but not substantially below 4 and heating under pressure to produce a temperature not greater than about 150° C. to produce a tannin-like material from such vegetable material. 2. Tannin-like material produced by the method of claim 1.

Synthetic Tanning Agents and Methods of Preparation and Use. U. S. Pat. 2,676,870. Robert C. Putnam, Marblehead, and Wilson M. Kleibacker, Salem Mass., assignors to United Shoe Machinery Corporation, Flemington, N. J., a corporation of New Jersey. Apl. October 24, 1951.



1. A process for forming tanning agents which comprises bringing together a polyhydric phenol with both an alkyl nitrile and hydrogen cyanide and causing them to react in the presence of hydrogen chloride.

Process of Making Light Colored and Light Stable Phenolic Syntans. U. S. Pat. 2,677,675. Daniel E. Nagy, Stamford, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine. Apl. August 9, 1949. 1. A process which consists of mixing a sulfonated product of the condensation of phenol and formaldehyde with a sufficient quantity of a substance of the group consisting of sulfur dioxide, sulfurous acid and water-soluble salts thereof to provide a free SO_2 concentration of at least about 0.5 part per thousand whereby the resulting composition is stable against discoloration upon storage under normal conditions.

Water-Resistant Animal Glue. U. S. Pat. 2,708,169. Harvard L. Keil, Clarendon Hills, and Louise K. Fencil, Chicago, Ill., assignors to Armour and Company, Chicago Ill., a corporation of Illinois. Apl. April 5, 1952. 1. In the preparation of a water resistant glue, the steps of treating solid, hydrated animal glue with an excess of carbon disulfide to decrease the reaction rate of the protein molecules in said glue with formaldehyde by blocking the free amino groups in said protein molecules, forming a viscous suspension of the treated glue in water, adding sufficient ethylene chorohydrin to said suspension to keep said suspension in fluid condition at room temperature, and finally mixing with said suspension a formaldehyde-liberating material providing about 10% by weight of formaldehyde compared to the weight of the glue solids.

Proofing Against Fungi and Insects. Brit. Pat. 648,518. Scientific Oil Compounding Co., Inc. Nov. 5, 1948. Porous materials such as wool, leather, and textiles are proofed against fungi and insects by impregnating them with a composition prepared by heating a water-insoluble soap of an alkaline earth metal, heavy metal or aluminum with an alkaline earth metal salt, heavy metal salt or aluminum salt of a hydroxy quinoline having a hydroxy

group or groups attached to the benzene nucleus of the quinoline radical. Specified soaps are the calcium, barium, magnesium, mercury, lead, cadmium, silver, thallium, manganese, cobalt, nickel, iron, copper, tin or aluminum soaps of caproic, caprylic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, ricinoleic, or naphthenic acids or mixtures of such soaps. Specified hydroxyquinoline salts are the 5-, 6-, 7- or 8-hydroxyquinoline salts of calcium, barium, magnesium, strontium, lead, mercury, manganese, cobalt, nickel, iron, copper, silver, thallium, tin, zinc or aluminum. The reaction may be effected at 200—550° F. or higher but below the decomposition temperature of the reactants. The reaction may be carried out in a reaction medium which may be an excess of the soap or a mixture of the soap with a higher fatty acid. Other specified reaction media are higher fatty acids, linseed oil, chinawood oil, cottonseed oil, soyabean oil, palm oil, coconut oil, sardine oil, tallow, lard, castor oil, dehydrated castor oil, tall oil, rosin, or abietic acid. The reaction products may be dispersed in oils, benzol, toluol, xylol, mineral spirits, fatty acids, carbon tetrachloride, coal tar solvents. Optional additions include phenolformaldehyde resins, rosin, kauri, copal, congal, ester gum, reaction products of rosin, maleic anhydride and a polyhydric alcohol, glycol, glycerin, pentaerythritol, sorbitol, mannitol, paraffin wax, beeswax, carnauba wax, spermaceti wax, candelilla wax. The hot liquid products may be used as impregnants.

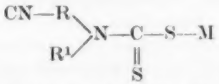
Furs; Proofing Permeabe Material. Brit. Pat. 649,974. Evans & Co., J. R. May 16, 1947. Furs such as lamb, sheep, goat, muskrat and fox skins are treated according to the process disclosed in the parent Specification with an acid-reacting aqueous solution of *p*H 0.3 to 3.0 containing free resorcinol or pyrogallol and a free aldehyde reactive therewith such as formaldehyde, polymers of formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde or furfural, both of which remain substantially unreacted at the beginning of the process. The weight of resorcinol or pyrogallol is 1 to 10 per cent, and preferably 5 to 7.5 per cent, by weight based on the wet material and the molecular ratio of aldehyde to resorcinol or pyrogallol is at least 2:1 and preferably between 2:1 and 6:1. In one example, sheepskins are placed in a liquor containing 10 per cent resorcinol, 20 per cent formaldehyde, sulphuric acid and salt at a *p*H 2.0 and paddled 10 mins. In the afternoon, after the morning soak, the *p* H is reduced to 1.5, the following morning to 1.0 and the succeeding afternoon to pH 0.5 to 0.6 by the addition of sulphuric acid followed by a short paddling period, whereafter the skins are paddled for about 1 minute each hour during the night. Subsequent treatment includes neutralizing washes with sodium bicarbonate solution and fat liquoring. The fats may be ironed at 200° F., if wet, or within the range 350° to 450° F.; if dry. If desired, the treated fur may be further treated with formaldehyde and then ironed hot until dry. The process is applicable to keratinous filaments such as hair and wool, as such or in the form of wool fabrics, which are stated to be thereby rendered more resistant to heat and to aqueous alkalies.

The Specification as open to inspection under Sect. 91 states that the resorcinol or pyrogallol may be wholly or in part replaced by nuclear substituted derivatives thereof, e.g. hexyl resorcinol, tertiary octyl resorcinol, benzyl resorcinol, phenyl resorcinol and methoxy resorcinol. This subject-matter does not appear in the Specification as accepted.

Lubricating Leather. Brit. Pat. 651,866. American Cyanamid Co. Feb. 12, 1948. Lubricated aluminum salt-containing leather is produced by impregnating with an aqueous fat-liquoring emulsion containing a cationic emulsifying agent in the presence of 1—10 per cent based on the weight of leather of a water-soluble salt of phthalic acid, e.g. the normal or acid phthalates of ammonium, sodium, potassium, or other alkali metal. The leather may be treated with the phthalate before or during fat-liquoring or both. Suitable emulsions contain olive oil, neatsfoot oil, coconut oil, or moellen degras with 10—30 per

cent cationic emulsifying agent such as an amide of sulphonated oleic acid, a product of condensation of 2—6 mols. ethylene oxide with 1 mol. octadecylguanidine acetate, N,N¹-di-octadecyl-beta-hydroxyethylimino dipropionamide, N,N¹-dimethyl-propylamine stearamide, di-stearyl-diethylene triamine condensed with 15 mols. ethylene oxide, or N,2-hydroxyethyl-beta-(octadecylamino) propionamide. An example describes the tanning of hides by drumming with melamine-formaldehyde resin polymerized with aluminum sulphate in the presence of disodium phthalate, sodium chloride, borax and water, followed by the fat-liquoring. Specification 569,385 is referred to.

Proofing Against Fungi. Brit Pat. 652,614. Monsanto Chemical Co. Sept. 23, 1947. A fungicidal composition for proofing textile materials, wood, or leather contains as an essential active ingredient a salt of an N-cyano alkyl substituted dithiocarbamic acid, a solvent liquid, suspension or emulsion as a carrier therefore, and wetting or dispersing agent. The active compounds have the formula



R being an alkeylne group, preferably ethylene, R^1 being an alkyl group which may be substituted, and is preferably substituted by a second N-cyano alkyl dithio-carbamate group and M being sodium potassium calcium, magnesium, zinc, copper, mercury or an amine. Many compounds are specified, the preferred being disodium or zinc ethylene-bis-(N-2- cyano ethyl-dithio-carbamate), and zinc N-ethyl-N-2-cyano ethyl dithio-carbamate. Specified wetting or dispersing agents are alkylated naphthalene sulphonic acid, soap, Turkey red oil and sodium salts of alkylated benzene sulphonic acids.

Leather Bleaching. Brit. Pat. 654,305. British Industrial Plastics, Ltd. Feb. 23, 1948. Water-soluble aminotriazine-aldehyde condensation products (*see* Group IV (a)), are used for improving the wet strength of paper or for bleaching leather. In example (5) bleached kraft pulp was dispersed in a beater and an aqueous syrup prepared by heating a melamine-formaldehyde condensation product with an alkali metal sulphite under alkaline conditions was added. 3 parts of resin solids were added per 100 parts of dry fibre. Sheets were prepared and cured at raised temperature. Example (8) describes treatment of chrome-tanned leather at 50° C. with a similar resin solution, followed by washing. A white skin is produced.

Fur Skins; Tanning. Brit. Pat. 655, 094. Aabye, J. S. F. April 30, 1948. Hides or skins, including fur skins, are subjected to partial tanning with known tanning agents and to subsequent freezing at, say, −10° or −30° C. with simultaneous or subsequent drying in the frozen condition. Drying may be at −2° C.

Ornamenting Leather. Brit. Pat. 656,267. Reptile Dressers, Ltd., and Smith, H. W. June 19, 1948. A pattern is applied to leather by coating the leather with an adhesive of a type which will remain flexible when dry, e.g. synthetic resin, cellulose lacquer, or gum drying the adhesive, applying to the adhesive-coated face of the leather a heat-fixing transfer, having an adhesive coating, carrying the desired pattern, the transfer being of a type which produces a flexible pattern coating on the leather, subjecting the leather and applied transfer to heat and pressure, e.g. 130° F. at 200 lbs./sq. inch for 5 secs., wetting and removing the transfer backing, and then drying and staking the leather. The surface may be subsequently sprayed or coated with a flexible cellulosic, albuminous, or casein lacquer, and the leather is then dried and finally glazed or plated or both.

Leather From Whale Hides. Brit. Pat. 656,848. Ben-Dixen, K. Dec. 16, 1947. Tanned hides of large whales, especially true whales, black whales, and finback whales e.g. the common finback whale or the blue whale, are prepared from hides including the fat-yielding tissues, so-called blubber which contains leather-forming fibres, by removing the epidermis and, before or after tanning, subjecting the hide to a compression at right angles to the surface at a moderate temperature preferably a temperature not exceeding 30° C., whereby the fatty substance or part thereof is pressed out without detrimentally influencing the hide fibres and the glue tissue, thus forming a raw hide or leather, the raw hide being afterwards converted into leather by tanning. The epidermis is removed by scraping the moist hide, which may have been preserved in salt. If the hide so scraped is then salted, the salt is removed before tanning. If desired, the tanned leather may be treated with a solvent, e.g. petrol to remove contingently remaining fatty substances. For chamois leather, compression is carried out during the fulling process.

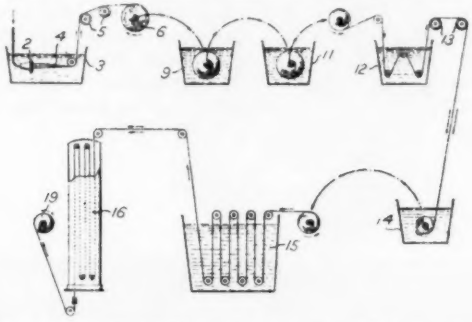
Softening Leather and Paper; Waterproofing. Brit. Pat. 657,419. Nopco Chemical Co. Feb. 27, 1948. Mixed fatty polyamides derived from polyamines acylated with a carboxylic acid containing 8—22 carbon atoms and a carboxylic acid containing 2—5 carbon atoms (for preparation *see* Group IV (b) Abridgment) may be used as softeners for paper, and lubricants and softeners for leather.

The Specification as open to inspection under Sect. 91 contains examples in which (22) cotton fabric is made waterproof by treatment with a 2 per cent aqueous dispersion of a stock emulsion obtained by gradually adding aqueous aluminum acetate to a molten mixture of paraffin wax and a condensation product of ethanol ethylene diamine with hydrogenated soyabean oil and acetic acid; (24) tissue paper is softened and made flexible by spraying prior to calendering with a 1 per cent solution of the hydroxy acetic acid salt of the condensation product of ethanol ethylene diamine (1 mol.), oleic acid (1 mol.) and acetic anhydride (½ mol.); and (25) an emulsion derived from neat's-foot oil and water using as emulsifying agent a hydroxy acetic acid solution of a mixed polyamide of ethanol ethylene diamine with refined corn syrup and acetic anhydride is used as a fat liquor for softening and lubricating alum tanned kid leather. This subject-matter does not appear in the Specification as accepted.

Carroting Furs. Brit. Pat. 657,493. American Hatters & Furriers Co., Inc. March 25, 1948. Fur fibres on or off the skin are carroted by treating in the presence of a source of active oxygen with an aqueous solution of nitric and nitrous acids containing (a) soluble salts of at least one, preferably two, radioactive elements; (b) a soluble salt of a polyvalent metal, the salts (a) and (b) being present in such proportion that the average overall atomic weight of the metals is 123—220; (c) a mineral acid hydrolyzing agent; and (d) a retarding agent comprising a water-soluble aliphatic acid. preferably with not more than 6 C atoms in the molecule and/or a water-soluble potassium salt. The radio-active elements may be uranium, thorium, polonium, actinium, plutonium, or protoactinium or their isotopes, preferably with a half-life of not less than 90 days, while the polyvalent metal may be barium, bismuth, cadmium, chromium, copper, iridium, manganese, molybdenum, palladium, rhodium, strontium, tantalum, tungsten, or vanadium, and the salts in both cases may be nitrates, sulphates, halides, phosphates, acetates, formates, or propionates. Suitable mineral acids are sulphuric, phosphoric, or hydrochloric, or mixtures thereof; the potassium salt may be the sulphate, phosphate, nitrate, bisulphate, bisulphite, hydrosulphite, or thiosulphate, while the organic acid may be formic, acetic, halogenacetic, propionic, halogenpropionic, succinic, malic, maleic, gluconic, glycollic, glutaric, citric, tartaric, or mixtures thereof. Examples of sources of active oxygen are hydrogen peroxide, hypochlorous, chloric, or perchloric acids in aqueous solution. Copper phthalocyanine or alizarine blue may be added during fur treatment to remove yellow colour.

Tanning Agents. Brit. Pat. 661,176. Plastica Soc. Annon. Dec. 31, 1947. A substance capable of use in the treatment of fibrous organic materials, e.g. as an assistant in tanning, leather-dressing, textile-dyeing and like operations, is prepared by concentrating whey or whey-like dispersions obtained as by-products in the manufacture of cheese or milk-sugar. The concentration may be carried on sufficiently to produce a salve-like product or a powder and may be effected in two stages. The albumen which separates may be removed or it can be broken down into simpler compounds by acidification of the whey with lactic acid or by bacterial action. The milk-sugar present can be partially split into galactose and glucose. A disinfectant, preferably one having a bleaching-action, such as a sulphite, and a preservative such as phenol, cresol, naphthol, chlorinated cresol, diphenyl oxide or etheric oil can be added. The sugar and albumen content can be increased by the addition, either before or after concentration, of glucose, galactose, or milk-sugar, or albumen or its decomposition products such as pure or chemically-modified amino acids. Oils and fats in emulsion or solution, sulphite waste liquor, or wetting-agents such as triethanolamine can also be included. The *p*H of the concentrate can be adjusted by the addition of acids or alkalies.

Collagen Strands. Brit. Pat. 663,032. American Cyanamid Co. Apl. April 8, 1947.



A collagen strand is rendered suitable as a suture material by treatment with a dilute solution of a tanning agent, softening the resulting lightly tanned strand with water or a dilute aqueous acid solution, stretching the strand and setting the stretch by treating the stretched strand with a relatively more concentrated solution of a tanning agent and/or a coagulating agent. The tanning agent used in the second treatment may be the same as, or different from, that used in the first treatment. According to the example, a collagen solution of *p*H 2 to 4 is extruded through a spinerette 2 into a coagulating bath 3 containing at least 35 per cent ammonium sulphate at a *p*H 7.8, preferably in the presence of a lubricant, e.g. vegetable oil. The strands 4 are stretched over the godets 5, spooled on 6 and, if desired, set in the bath 9 containing at least 35 per cent aqueous ammonium sulphate. The set strands are pretanned for 24 hours in a bath 11 containing 0.05 per cent chromic sulphate (as Cr_2O_3) at *p*H 4.8 and at least 35 per cent ammonium sulphate, softened in water or dilute acid 12, stretched over godets 13, given a final tanning in a bath 14 containing 2.5 per cent Cr_2O_3 at *p*H 3.8 and 10 per cent sodium sulphate, washed in water 15, dried in chamber 16 at 60° C. and finally wound on spool 19. Generally 0.01 to 0.50 per cent Cr_2O_3 may be used in the pre-tanning stage and 1.0 to 10 per cent Cr_2O_3 in the final tanning stage.While any conventional tanning agent may be used, formaldehyde, ferric and aluminum salts are preferred in addition to the chromium salts specified above. Organic coagulants such as water-soluble ketones, alcohols and ethers may be employed but inor-

ganic coagulants such as sodium, magnesium and ammonium sulphates are preferred. Pretanning solutions are substantially saturated with respect to the coagulants but lower concentrations, e.g. 10 per cent by weight, may be used in the final tanning stage. 15 to 25 per cent, preferably 20 per cent, solutions of coagulants are employed in the softening stage. The strand may be formed by the extrusion of melted collagen.

Making Leather. Brit. Pat. 666,619. Forestal Land, Timber & Railway Co., Ltd. Sept. 27, 1950. Hides and skins (especially split hides, ox hides, and sheepskins) are converted into leather by impregnation with a substantially non-resinous condensation product of one or more aldehydes with one or more ketones, followed by treatment with an alkaline solution to resinify the condensation product. Alternatively the hides may be impregnated with a solution or dispersion of a water-insoluble resin formed from the condensation product. The hides may be immersed in the undiluted liquid products or in their aqueous solutions or dispersions (using, e.g., sulphonated castor oil as a dispersing agent); the resins are dissolved in liquid condensation products or in aqueous ethyl alcohol; treatment is for 3 days at room temperature or for a shorter period when the hides are drummed or a dispersing agent is used. The alkaline solution preferably has a *p*H greater than 11; a 10 per cent solution of sodium carbonate or a solution of sodium hydroxide containing sodium carbonate or neutral salts may be used. The condensation products are formed by reacting formaldehyde, acetaldehyde, and crotonaldehyde with acetone, methyl ethyl ketone, and methyl propyl ketone in the presence of methyl alcoholic potash or sodium carbonate (*see* Group IV (a). Limed hides may be delimed during impregnation by adding an acid or ammonium chloride to the condensation product. The resulting leather may be oiled or filled with vegetable tans.

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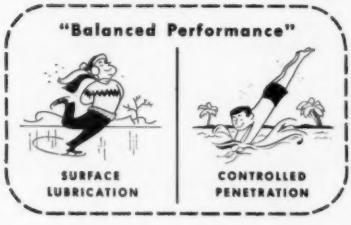

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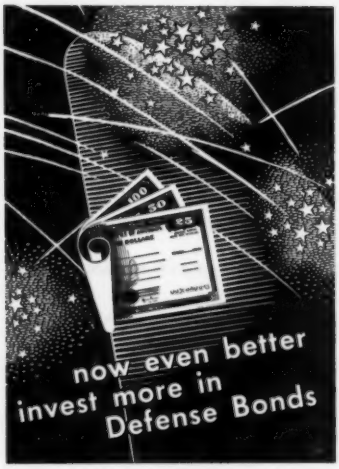

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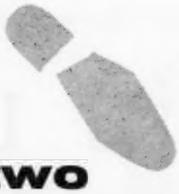

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